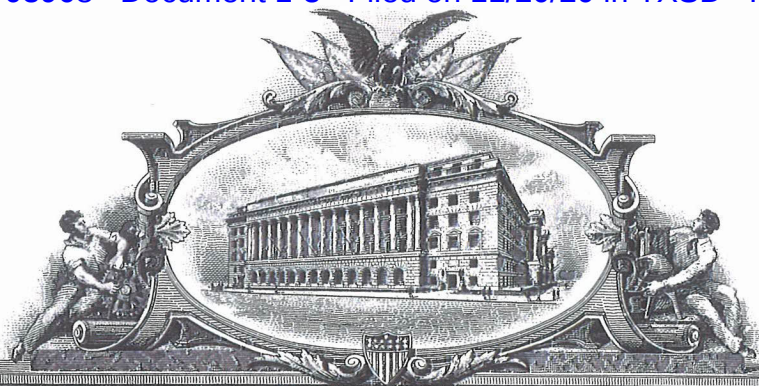


# **Exhibit B**

U 8028666



# THE UNITED STATES OF AMERICA

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**December 23, 2019**

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**U.S. PATENT: 10,507,565**

**ISSUE DATE: December 17, 2019**

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(12) **United States Patent**  
**Bertagnolli et al.**

(10) **Patent No.: US 10,507,565 B2**(45) **Date of Patent: \*Dec. 17, 2019**

(54) **POLYCRYSTALLINE DIAMOND,  
POLYCRYSTALLINE DIAMOND  
COMPACTS, METHODS OF MAKING SAME,  
AND APPLICATIONS**

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(\*) Notice: Subject to any disclaimer, the term of this  
patent is extended or adjusted under 35  
U.S.C. 154(b) by 0 days.

This patent is subject to a terminal dis-  
claimer.

(21) Appl. No.: **15/080,379**

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(51) **Int. Cl.**  
**B24D 3/10** (2006.01)  
**E21B 10/567** (2006.01)  
(Continued)

(52) **U.S. Cl.**  
CPC ..... **B24D 3/10** (2013.01); **C22C 26/00**  
(2013.01); **E21B 10/567** (2013.01);  
(Continued)

(58) **Field of Classification Search**  
CPC ..... B24D 3/10; F16C 33/043; E21B 10/567  
See application file for complete search history.

(56) **References Cited**

**U.S. PATENT DOCUMENTS**

3,101,260 A 8/1963 Cheney  
3,141,746 A 7/1964 De Lai  
(Continued)

**FOREIGN PATENT DOCUMENTS**

CN 1249221 4/2000  
CN 101321714 12/2008  
(Continued)

**OTHER PUBLICATIONS**

U.S. Appl. No. 12/608,155, filed Oct. 29, 2009, Sani.  
(Continued)

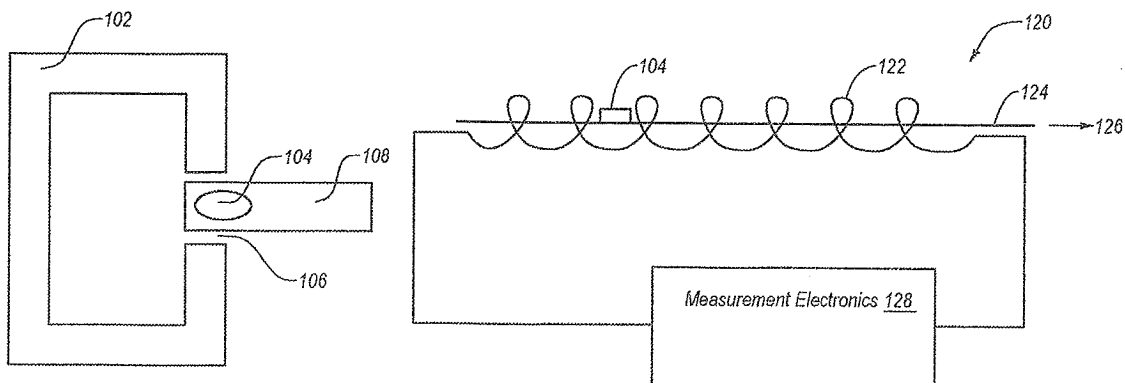
*Primary Examiner* — Shuangyi Abu Ali

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(57) **ABSTRACT**

Embodiments of the invention relate to polycrystalline diamond compacts ("PDC") exhibiting enhanced diamond-to-diamond bonding. In an embodiment, a PDC includes a polycrystalline diamond ("PCD") table bonded to a substrate. At least a portion of the PCD table includes a plurality of diamond grains defining a plurality of interstitial regions. The plurality of interstitial regions includes a metal-solvent catalyst. The plurality of diamond grains exhibit an average grain size of about 30  $\mu\text{m}$  or less. The plurality of diamond grains and the metal-solvent catalyst collectively exhibit an average electrical conductivity of less than about 1200 S/m. Other embodiments are directed to PCD, employing such PCD, methods of forming PCD and PDCs, and various

(Continued)



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applications for such PCD and PDCs in rotary drill bits, bearing apparatuses, and wire-drawing dies.

## 33 Claims, 17 Drawing Sheets

## Related U.S. Application Data

continuation-in-part of application No. 12/858,906, filed on Aug. 18, 2010, now Pat. No. 9,459,236, which is a division of application No. 12/244,960, filed on Oct. 3, 2008, now Pat. No. 7,866,418.

## (51) Int. Cl.

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*C22C 26/00* (2006.01)  
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*F16C 17/02* (2006.01)  
*F16C 17/04* (2006.01)

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CPC ..... *F16C 33/043* (2013.01); *F16C 33/26* (2013.01); *B22F 2005/001* (2013.01); *F16C 17/02* (2013.01); *F16C 17/04* (2013.01); *F16C 2352/00* (2013.01)

## (56)

## References Cited

## U.S. PATENT DOCUMENTS

3,574,580 A	4/1971	Stromberg et al.	6,189,634 B1	2/2001	Bertagnolli et al.
3,829,544 A	8/1974	Hall	6,220,375 B1	4/2001	Butcher et al.
3,909,647 A	9/1975	Peterson	6,227,318 B1	5/2001	Siracki
4,268,276 A	5/1981	Bovenkerk	6,241,035 B1	6/2001	Portwood
4,403,015 A	9/1983	Nakai et al.	6,290,008 B1	9/2001	Portwood et al.
4,410,054 A	10/1983	Nagel et al.	6,338,754 B1	1/2002	Cannon et al.
4,425,315 A	1/1984	Tsuji et al.	6,342,301 B1	1/2002	Yoshida et al.
4,468,138 A	8/1984	Nagel	6,408,959 B2	6/2002	Bertagnolli et al.
4,525,178 A	6/1985	Hall	6,443,248 B2	9/2002	Yong et al.
4,560,014 A	12/1985	Geczy	6,460,637 B1	10/2002	Siracki et al.
4,604,106 A	8/1986	Hall et al.	6,555,234 B2	12/2003	Scott
4,610,600 A	9/1986	Bleier	6,749,033 B2 *	6/2004	Griffin ..... C04B 37/021
4,610,699 A	9/1986	Yazu et al.			175/428
4,636,253 A	1/1987	Nakai et al.	6,793,681 B1	9/2004	Pope et al.
4,643,741 A *	2/1987	Yu ..... B01J 3/062	6,913,633 B2	7/2005	Fries et al.
		51/295	6,915,866 B2	7/2005	Middlemiss
4,694,918 A	9/1987	Hall	6,987,318 B2	1/2006	Sung
4,738,322 A	4/1988	Hall et al.	7,108,598 B1	9/2006	Galloway
4,729,440 A	5/1988	Hall	7,216,661 B2	5/2007	Welty et al.
4,811,801 A	3/1989	Salesky et al.	7,350,601 B2	4/2008	Belnap et al.
4,913,247 A	4/1990	Jones	7,435,478 B2	10/2008	Keshavan
5,016,718 A	5/1991	Tandberg et al.	7,462,003 B2	12/2008	Middlemiss
5,092,687 A	3/1992	Hall	7,493,972 B1	2/2009	Schmidt et al.
5,120,327 A	6/1992	Dennis	7,516,804 B2	4/2009	Vail
5,135,061 A	8/1992	Newton, Jr. et al.	7,517,589 B2	4/2009	Eyre
5,151,107 A	9/1992	Cho et al.	7,543,662 B2	6/2009	Belnap et al.
5,154,245 A	10/1992	Waldenstrom et al.	7,552,782 B1	6/2009	Sexton et al.
5,355,969 A	10/1994	Hardy et al.	7,559,695 B2	7/2009	Sexton et al.
5,364,192 A	11/1994	Damm et al.	7,575,805 B2	8/2009	Achilles et al.
5,368,398 A	11/1994	Damm et al.	7,628,234 B2	12/2009	Middlemiss
5,370,195 A	12/1994	Keshavan et al.	7,740,673 B2	6/2010	Eyre
5,460,233 A	10/1995	Meany et al.	7,757,791 B2	7/2010	Belnap et al.
5,469,927 A	11/1995	Griffin	7,866,418 B2 *	1/2011	Bertagnolli ..... 175/328
5,480,233 A	1/1996	Cunningham	8,020,645 B2	9/2011	Bertagnolli et al.
5,544,713 A	8/1996	Dennis	8,158,258 B2 *	4/2012	Bertagnolli ..... C22C 26/00
5,605,199 A	2/1997	Newton			428/325
5,769,176 A	6/1998	Sumiya et al.	8,197,936 B2	6/2012	Keshavan
5,848,348 A	12/1998	Dennis	8,236,074 B1	8/2012	Bertagnolli et al.
5,875,862 A	3/1999	Jurewicz et al.	8,297,382 B2 *	10/2012	Bertagnolli ..... B22F 7/08
5,889,219 A	3/1999	Moriguchi et al.			175/328
6,090,343 A	7/2000	Kear et al.	8,461,832 B2	6/2013	Bertagnolli et al.
6,132,675 A	10/2000	Corrigan et al.	8,616,306 B2 *	12/2013	Bertagnolli ..... B22F 7/08
6,145,607 A	11/2000	Griffin et al.			175/328
			8,727,046 B2 *	5/2014	Miess ..... B01J 3/062
					175/420.2
			8,766,628 B2	7/2014	Bertagnolli et al.
			9,315,881 B2 *	4/2016	Bertagnolli ..... C22C 26/00
			9,932,274 B2 *	4/2018	Bertagnolli ..... C22C 26/00
			2002/0071729 A1	6/2002	Middlemiss et al.
			2004/0062928 A1	4/2004	Raghavan et al.
			2004/0140132 A1	7/2004	Middlemiss
			2005/0050801 A1	3/2005	Cho et al.
			2005/0139397 A1	6/2005	Achilles et al.
			2005/0210755 A1	9/2005	Cho et al.
			2005/0262774 A1	12/2005	Eyre et al.
			2006/0038156 A1	2/2006	Welty et al.
			2006/0060392 A1	3/2006	Eyre
			2006/0157285 A1	7/2006	Cannon et al.
			2006/0162969 A1 *	7/2006	Belnap ..... B22F 7/06
					175/433
			2006/0165993 A1	7/2006	Keshavan
			2006/0180354 A1	8/2006	Belnap et al.
			2006/0266558 A1	11/2006	Middlemiss et al.
			2007/0014965 A1	1/2007	Chodelka et al.
			2007/0079994 A1	4/2007	Middlemiss
			2007/0187155 A1	4/2007	Middlemiss
			2007/0181348 A1	8/2007	Lancaster et al.
			2007/0205023 A1	9/2007	Hoffmaster et al.
			2008/0022806 A1	1/2008	Sumiya
			2008/0023231 A1	1/2008	Vail
			2008/0115424 A1	5/2008	Can et al.
			2008/0142276 A1	6/2008	Griffo et al.
			2008/0178535 A1	7/2008	Wan
			2008/0185189 A1	8/2008	Griffo et al.
			2008/0206576 A1	8/2008	Qian et al.
			2008/0302579 A1	12/2008	Keshavan et al.
			2009/0152018 A1	6/2009	Sani
			2009/0208301 A1	8/2009	Kuroda et al.
			2010/0112332 A1	5/2010	Kuroda et al.



## US 10,507,565 B2

Page 3

(56)

## References Cited

## U.S. PATENT DOCUMENTS

2010/0186304 A1 7/2010 Burgess et al.  
 2010/0242375 A1 9/2010 Hall et al.  
 2010/0307069 A1 12/2010 Bertagnolli et al.  
 2010/0330357 A1 12/2010 Davies et al.  
 2011/0017517 A1 1/2011 Scott et al.  
 2011/0031032 A1 2/2011 Mourik et al.  
 2011/0031033 A1 2/2011 Mourik et al.  
 2011/0031037 A1 2/2011 Bellin et al.  
 2011/0042147 A1 2/2011 Fang et al.  
 2011/0042149 A1 2/2011 Scott et al.  
 2011/0072730 A1 3/2011 Sithebe  
 2011/0083908 A1 4/2011 Shen et al.  
 2011/0189468 A1 8/2011 Bertagnolli et al.  
 2011/0192652 A1 8/2011 Shen et al.  
 2012/0241226 A1 9/2012 Bertagnolli et al.  
 2012/0261197 A1 10/2012 Miess et al.  
 2013/0187642 A1 7/2013 Bertagnolli et al.  
 2013/0205677 A1 8/2013 Bertagnolli et al.  
 2013/0264125 A1 10/2013 Miess et al.  
 2014/0215926 A1 8/2014 Miess et al.  
 2019/0211629 A1 7/2019 Bertagnolli et al.

## FOREIGN PATENT DOCUMENTS

EP	0462955	12/1991
GB	2384260	7/2003
JP	121251	6/1985
WO	WO 04/106004	12/2004
WO	WO 06/099194	9/2006
WO	WO 07/020518	2/2007
WO	WO 2011/011290	1/2011
WO	WO 2011/017592	2/2011

## OTHER PUBLICATIONS

U.S. Appl. No. 12/830,878, filed Jul. 6, 2010, Wiggins et al.  
 U.S. Appl. No. 13/275,372, filed Oct. 18, 2011, Mukhopadhyay.  
 U.S. Appl. No. 13/648,913, filed Oct. 10, 2012, Mukhopadhyay.  
 U.S. Appl. No. 14/246,657, filed Apr. 7, 2014, Miess, et al.  
 D.L. Decker, W.A. Basset, L. Merrill, H.T. Hall, and J.D. Barnett; "High-Pressure Calibration A Critical Review", J. Phys. Chem. Ref. Data, vol. 1, No. 3 (1972).  
 ASTM B887-03 (2008) "Standard Test Method for Determination of Coercivity (H<sub>cs</sub>) of Cemented Carbides".  
 ASTM B886-03 (2008), "Standard Test Method for Determination of Magnetic Saturation (M<sub>s</sub>) of Cemented Carbides".  
 W. Utsumi, N. Toyama, S. Endo, and F.E. Fujita, "X-ray diffraction under ultrahigh pressure generated with sintered diamond anvils", J. Appl. Phys., 60, 2201 (1986).  
 G. Rousse, S. Klotz, A.M. Saitta, J. Rodriguez-Carvajal, M.I. McMahon, B. Couzinet, and M. Mezouar, "Structure of the Intermediate Phase of PbTe at High Pressure", Physical Review B: Condensed Matter and Materials Physics, 71, 224116 (2005).  
 Tze-Pin Lin, Michael Hood, George A. Cooper, and Redd H. Smith, Residual Stresses in Polycrystalline Diamond Compacts, J. Am. Ceram. Soc. 77[6] pp. 1562-1568 (1994).  
 DR Moyle, ER Kimmel "Utilization of magnetic saturation measurements for carbon control in cemented carbides" Dec. 1984, American Society of Metals Metals/Materials Technology series 1984 ASM/SCITE conference on technology advancements in cemented carbide production 8415-009.  
 Akashi et al.; "Synthesis of Sintered Diamond with High Electrical Resistivity and Hardness"; J. Am. Ceram. Soc.; vol. 70, No. 10; 1987; pp. C-237-X-239.  
 Bochechka et al.; "The Study of HP-HT Interaction between Co-Base Melts and Diamond Powders"; High Pressure Chemical Engineering; 1996; p. 457.  
 Ekimov et al.; "Sintering of a Nanodiamond in the Presence of Cobalt"; Inorganic Materials; vol. 45, No. 5; 2009; pp. 491-494.  
 Godick; "Message from Neil B. Godick"; PHLburg Technologies, Inc.; Oct. 2008.

Osipov et al.; "A contribution to the study of the diamond solid state sintering."; Ceramica; vol. 49; 2003; pp. 151-157.

Shige et al.; "Sintering of Diamond Powder Electroless-Plated with Co Metal", Science and Technology of New Diamond, pp. 251-255 (1990).

Tardim; "A Novel Method for Obtaining Polycrystalline Diamond Cutters"; Materials Science Forum; vols. 660-661; 2010; pp. 477-482.

German; "Particle Packing Characteristics", Metal Powder Industries Federation; pp. 101-103; 1989 (6 pages).

International Search Report and Written Opinion from International Application No. PCT/US2009/054398 dated Feb. 2, 2010.

International Search Report and Written Opinion from International Application PCT/US2010/059619 dated Mar. 4, 2011.

U.S. Appl. No. 12/244,960, Apr. 27, 2010, Restriction Requirement.

U.S. Appl. No. 12/244,960, Jun. 16, 2010, Office Action.

U.S. Appl. No. 12/244,960, Sep. 27, 2010, Notice of Allowance.

U.S. Appl. No. 12/244,960, Nov. 29, 2010, Notice of Allowance.

U.S. Appl. No. 12/244,960, Dec. 22, 2010, Issue Notification.

U.S. Appl. No. 12/690,998, Feb. 27, 2012, Office Action.

U.S. Appl. No. 12/690,998, Jul. 17, 2012, Notice of Allowance.

U.S. Appl. No. 12/690,998, Oct. 10, 2012, Issue Notification.

U.S. Appl. No. 12/785,014, Sep. 10, 2012, Restriction Requirement.

U.S. Appl. No. 12/785,014, Feb. 5, 2013, Notice of Allowance.

U.S. Appl. No. 12/785,014, May 22, 2013, Issue Notification.

U.S. Appl. No. 12/858,906, Oct. 5, 2012, Office Action.

U.S. Appl. No. 12/858,906, Apr. 10, 2013, Office Action.

U.S. Appl. No. 12/858,906, Jul. 7, 2014, Office Action.

U.S. Appl. No. 12/858,906, Jan. 22, 2015, Office Action.

U.S. Appl. No. 12/858,906, May 18, 2015, Office Action.

U.S. Appl. No. 12/858,906, Oct. 7, 2015, Office Action.

U.S. Appl. No. 12/858,906, Dec. 23, 2015, Office Action.

U.S. Appl. No. 12/858,949, Dec. 23, 2010, Office Action.

U.S. Appl. No. 12/858,949, Jun. 8, 2011, Office Action.

U.S. Appl. No. 12/858,949, Jul. 28, 2011, Notice of Allowance.

U.S. Appl. No. 12/858,949, Aug. 31, 2011, Issue Notification.

U.S. Appl. No. 12/846,604, Aug. 8, 2011, Office Action.

U.S. Appl. No. 12/846,604, Feb. 27, 2012, Notice of Allowance.

U.S. Appl. No. 12/846,604, Mar. 28, 2012, Issue Notification.

U.S. Appl. No. 13/085,689, Mar. 15, 2013, Office Action.

U.S. Appl. No. 13/085,689, Jul. 17, 2013, Office Action.

U.S. Appl. No. 13/085,689, Oct. 30, 2013, Office Action.

U.S. Appl. No. 13/085,689, Jul. 3, 2014, Office Action.

U.S. Appl. No. 13/085,689, Jan. 22, 2015, Office Action.

U.S. Appl. No. 13/085,689, May 7, 2015, Notice of Allowance.

U.S. Appl. No. 13/085,689, Aug. 26, 2015, Issue Notification.

U.S. Appl. No. 13/486,578, Sep. 20, 2013, Restriction Requirement.

U.S. Appl. No. 13/486,578, Jan. 13, 2014, Office Action.

U.S. Appl. No. 13/486,578, Jul. 8, 2014, Office Action.

U.S. Appl. No. 13/486,578, Oct. 24, 2014, Office Action.

U.S. Appl. No. 13/486,578, May 7, 2015, Office Action.

U.S. Appl. No. 13/486,578, Sep. 25, 2015, Office Action.

U.S. Appl. No. 13/486,578, Dec. 11, 2015, Notice of Allowance.

U.S. Appl. No. 13/623,764, Jan. 14, 2013, Office Action.

U.S. Appl. No. 13/623,764, Apr. 16, 2013, Notice of Allowance.

U.S. Appl. No. 13/623,764, Jul. 29, 2013, Notice of Allowance.

U.S. Appl. No. 13/623,764, Dec. 11, 2013, Issue Notification.

U.S. Appl. No. 13/790,172, May 15, 2013, Office Action.

U.S. Appl. No. 13/790,172, Oct. 21, 2013, Office Action.

U.S. Appl. No. 13/790,172, Feb. 19, 2014, Notice of Allowance.

U.S. Appl. No. 13/790,172, Jun. 11, 2014, Issue Notification.

U.S. Appl. No. 13/087,775, Sep. 20, 2013, Office Action.

U.S. Appl. No. 13/087,775, Jan. 7, 2014, Notice of Allowance.

U.S. Appl. No. 13/087,775, Apr. 30, 2014, Issue Notification.

U.S. Appl. No. 13/789,099, Nov. 20, 2013, Office Action.

U.S. Appl. No. 13/789,099, Apr. 23, 2014, Office Action.

U.S. Appl. No. 13/789,099, Oct. 23, 2014, Office Action.

U.S. Appl. No. 13/789,099, May 13, 2015, Office Action.

U.S. Appl. No. 13/909,193, Sep. 18, 2015, Office Action.

U.S. Appl. No. 13/909,193, Feb. 18, 2016, Office Action.

U.S. Appl. No. 12/961,787, filed Dec. 7, 2010, Mukhopadhyay, et al.

U.S. Appl. No. 13/027,954, filed Feb. 15, 2011, Miess, et al.

## US 10,507,565 B2

Page 4

(56)

## References Cited

## OTHER PUBLICATIONS

- U.S. Appl. No. 13/037,548, filed Mar. 1, 2011, Gonzalez, et al.  
 U.S. Appl. No. 61/768,812, filed Feb. 25, 2013, Mukhopadhyay, et al.  
 U.S. Appl. No. 13/795,027, Mar. 12, 2013, Mukhopadhyay, et al.  
 U.S. Appl. No. 15/238,475, filed Aug. 16, 2016, Bertagnolli, et al.  
 U.S. Appl. No. 12/858,906, Apr. 7, 2016, Office Action.  
 U.S. Appl. No. 12/858,906, Aug. 2, 2016, Notice of Allowance.  
 U.S. Appl. No. 12/858,906, Sep. 2, 2016, Notice of Allowance.  
 U.S. Appl. No. 12/858,906, Sep. 14, 2016, Issue Notification.  
 U.S. Appl. No. 13/486,578, Mar. 30, 2016, Issue Notification.  
 U.S. Appl. No. 13/789,099, May 19, 2016, Examiner's Answer.  
 U.S. Appl. No. 13/909,193, Jun. 28, 2016, Office Action.  
 U.S. Appl. No. 13/909,193, Oct. 7, 2016, Advisory Action.  
 U.S. Appl. No. 14/246,657, May 18, 2016, Office Action.  
 U.S. Appl. No. 13/919,142, Aug. 24, 2015, Restriction Requirement.  
 U.S. Appl. No. 13/919,142, Apr. 7, 2016, Office Action.  
 U.S. Appl. No. 15/238,475, Sep. 29, 2016, Office Action.  
 U.S. Appl. No. 13/789,099, Oct. 2, 2017, Decision on Appeal.  
 U.S. Appl. No. 15/238,475, Dec. 29, 2017, Notice of Allowance.  
 U.S. Appl. No. 13/909,193, Jan. 6, 2017, Advisory Action.  
 U.S. Appl. No. 13/909,193, Feb. 2, 2017, Office Action.  
 U.S. Appl. No. 14/246,657, Jun. 12, 2017, Office Action.  
 U.S. Appl. No. 15/238,475, Jan. 12, 2017, Office Action.  
 U.S. Appl. No. 15/238,475, Apr. 24, 2017, Advisory Action.  
 U.S. Appl. No. 13/909,193, Oct. 6, 2017, Office Action.  
 U.S. Appl. No. 14/246,657, Oct. 20, 2017, Advisory Action.  
 U.S. Appl. No. 14/246,657, Nov. 24, 2017, Office Action.  
 U.S. Appl. No. 15/901,124, Feb. 21, 2018, Bertagnolli, et al.  
 U.S. Appl. No. 13/789,099, Feb. 26, 2018, Office Action.  
 U.S. Appl. No. 15/238,475, Mar. 14, 2018, Issue Notification.  
 U.S. Appl. No. 61/232,122, filed Aug. 7, 2009, Mourik et al.  
 U.S. Appl. No. 13/789,099, Oct. 16, 2018, Office Action.  
 U.S. Appl. No. 13/789,099, Jan. 4, 2019, Notice of Allowance.  
 U.S. Appl. No. 14/246,657, Sep. 14, 2018, Office Action.  
 U.S. Appl. No. 16/358,281, Mar. 19, 2019, Bertagnolli, et al.  
 Kletetschka et al., "Magnetic properties of aggregate polycrystalline diamond: implications for carbonado history" Earth and Planetary Science Letters 181 (2000) 279-290.  
 U.S. Appl. No. 13/789,099, Apr. 8, 2019, Supplemental Notice of Allowance.  
 U.S. Appl. No. 13/789,099, Apr. 24, 2019, Issue Notification.  
 U.S. Appl. No. 14/246,657, Mar. 8, 2019, Notice of Allowance.  
 U.S. Appl. No. 14/246,657, Jun. 14, 2019, Supplemental Notice of Allowance.  
 U.S. Appl. No. 14/246,657, Jun. 26, 2019, Issue Notification.  
 U.S. Appl. No. 16/358,281, Jun. 10, 2019, Office Action.  
 U.S. Appl. No. 15/901,124, Aug. 8, 2019, Office Action.  
 U.S. Appl. No. 16/358,281, dated Sep. 16, 2019, Notice of Allowance.

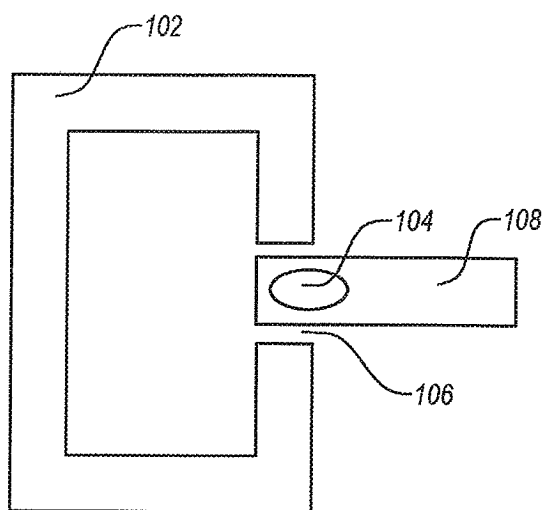
\* cited by examiner

**U.S. Patent**

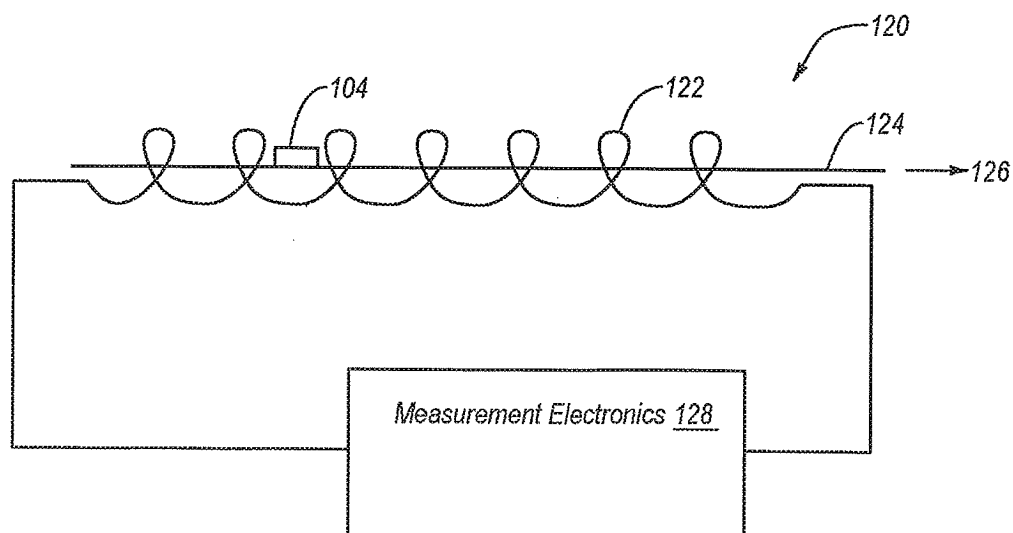
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**FIG. 1A**



**FIG. 1B**

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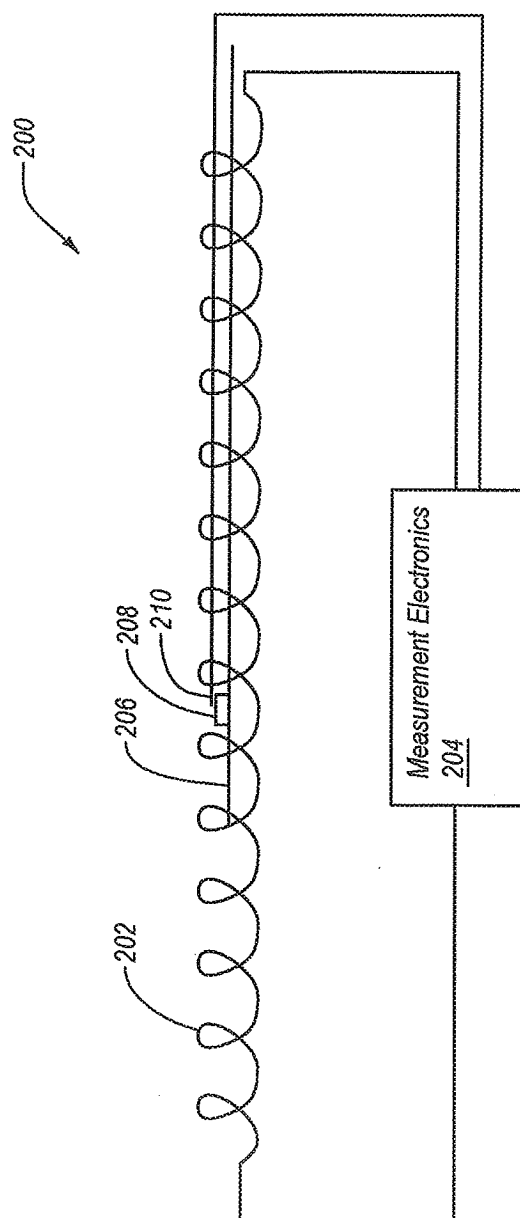


FIG. 2



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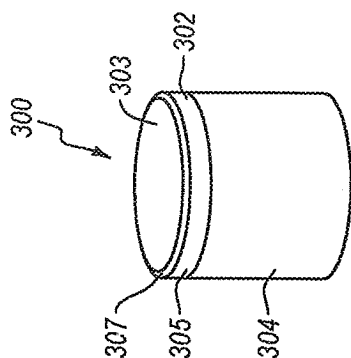


FIG. 3A

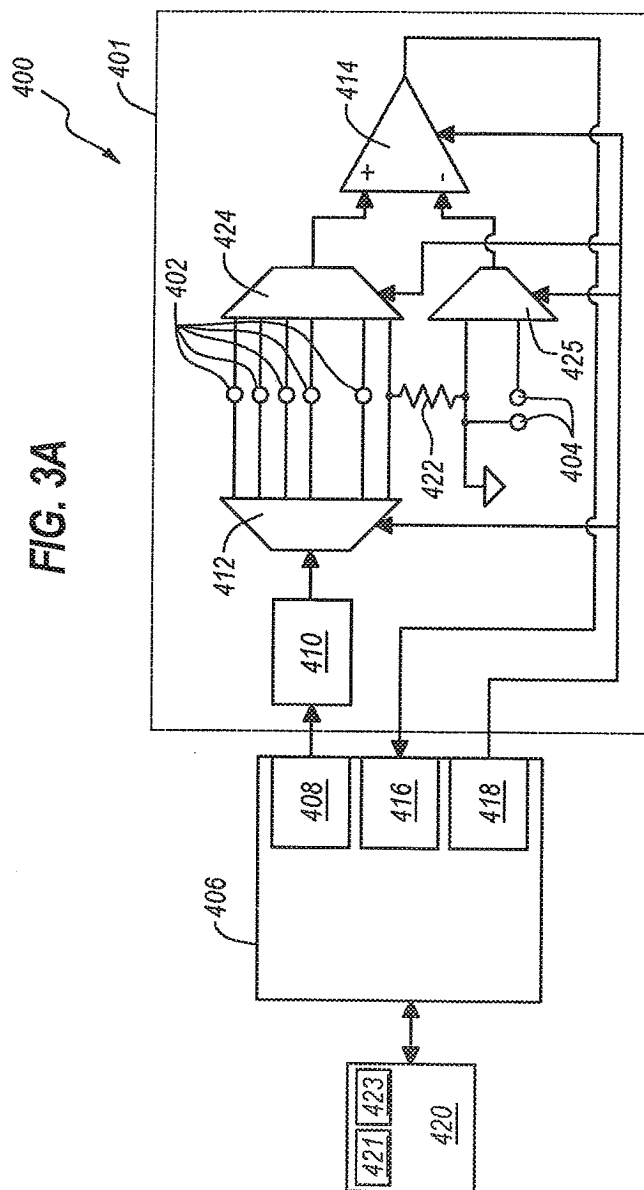


FIG. 3B

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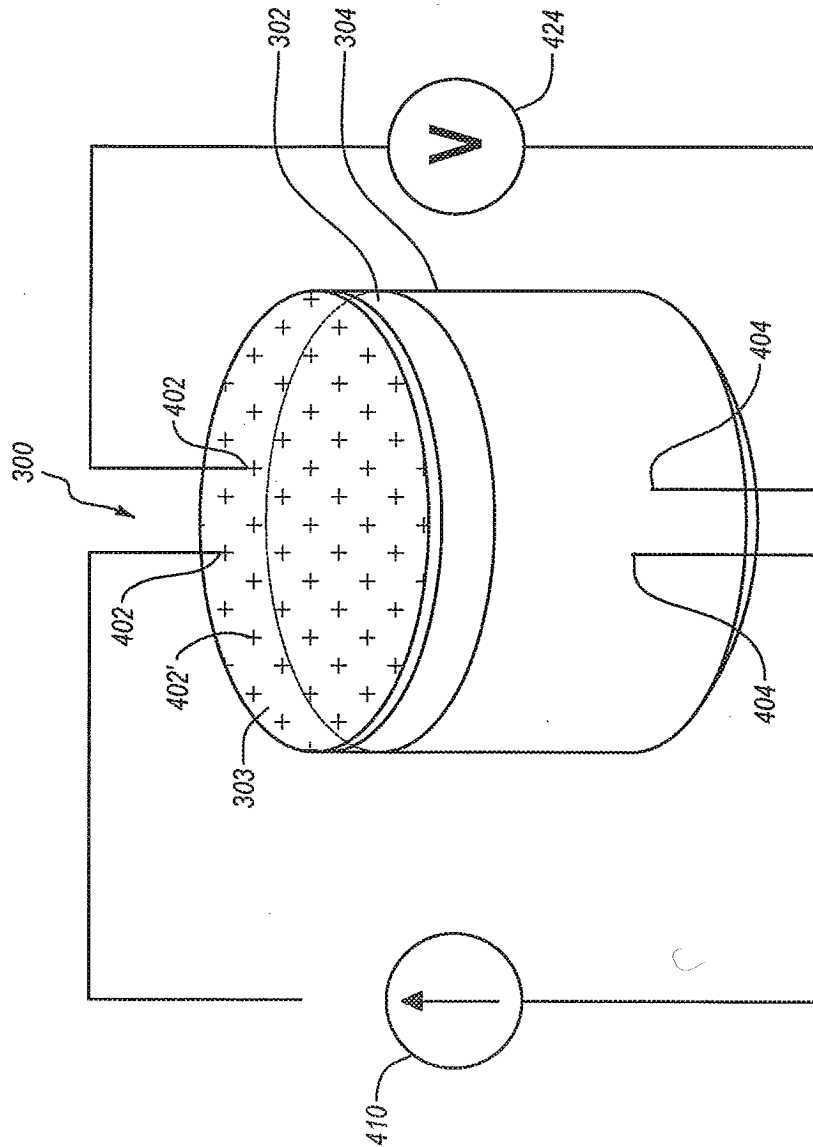


FIG. 4

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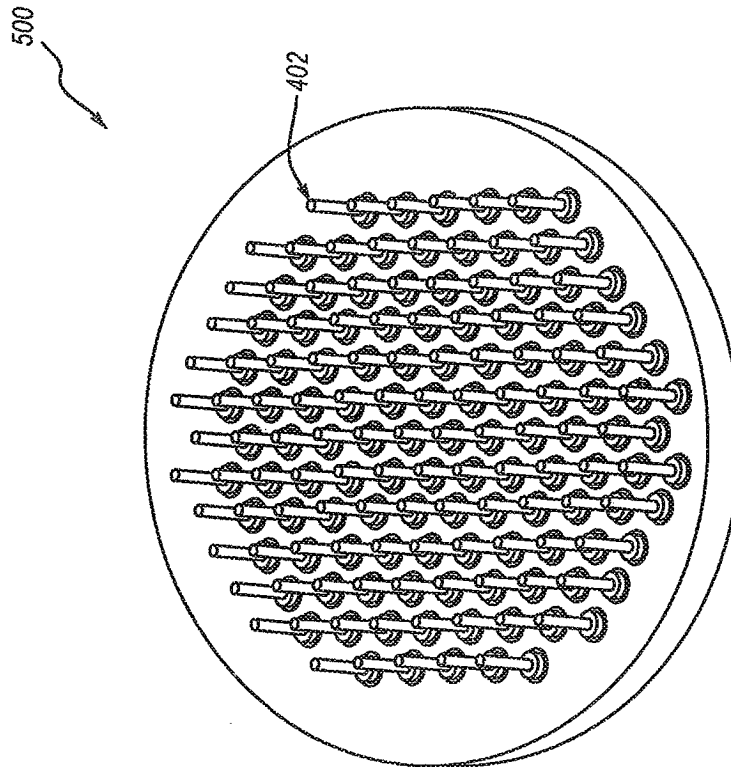


FIG. 5

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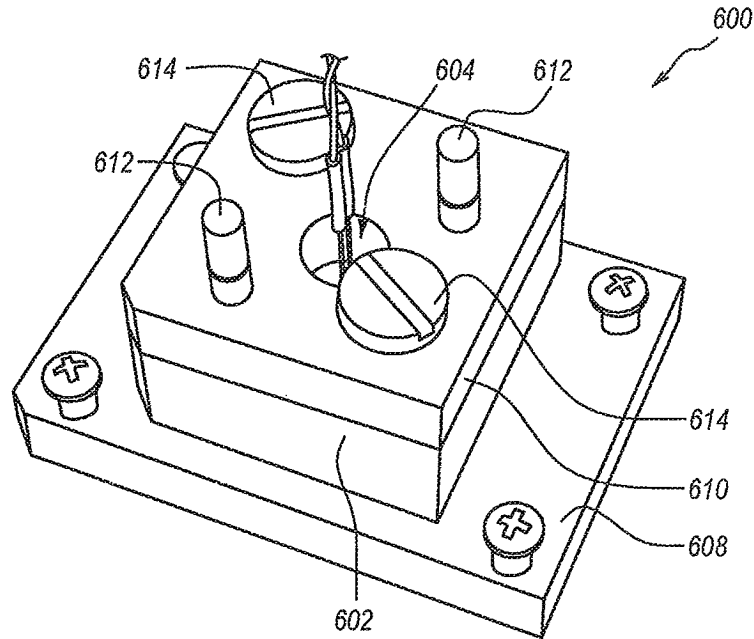


FIG. 6A

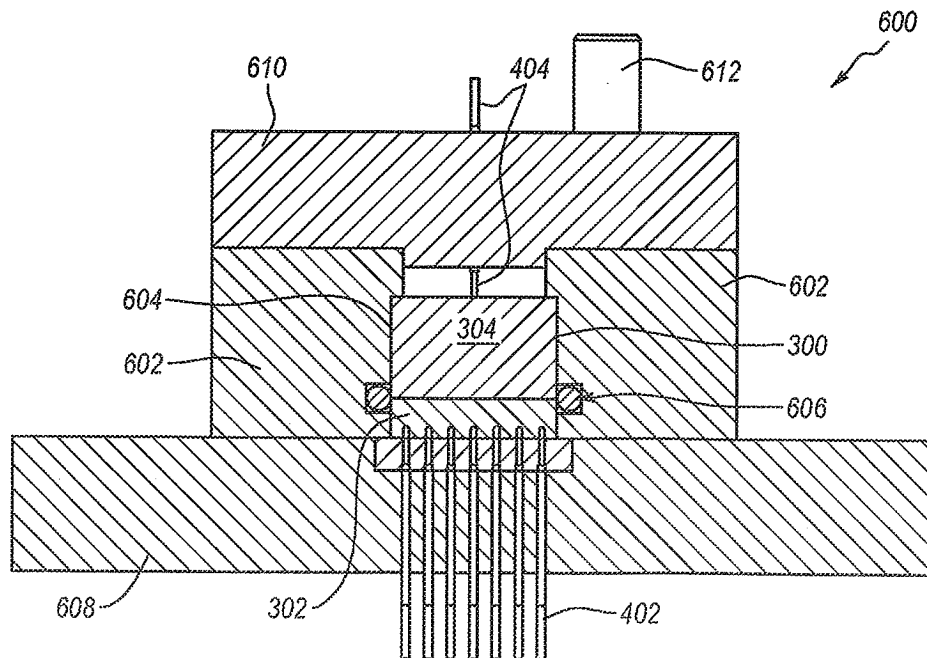
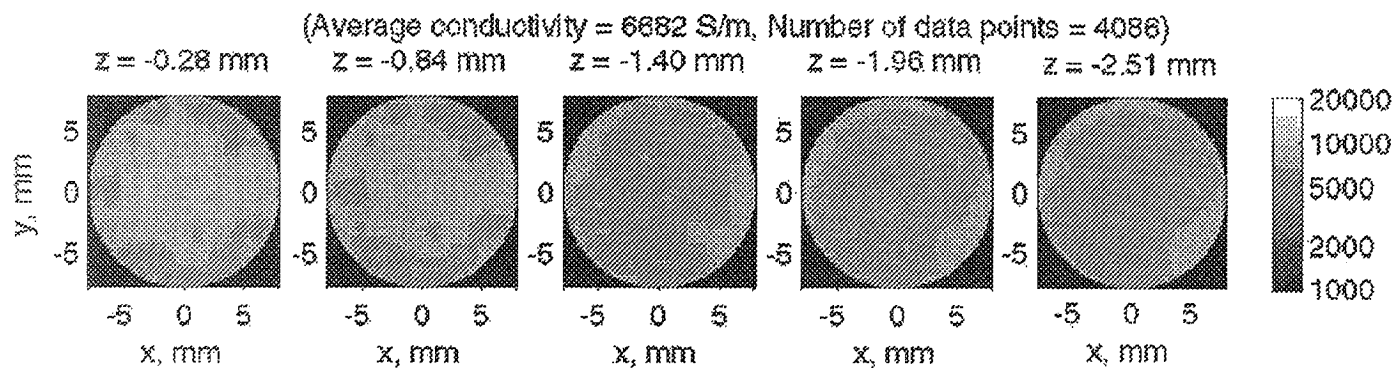
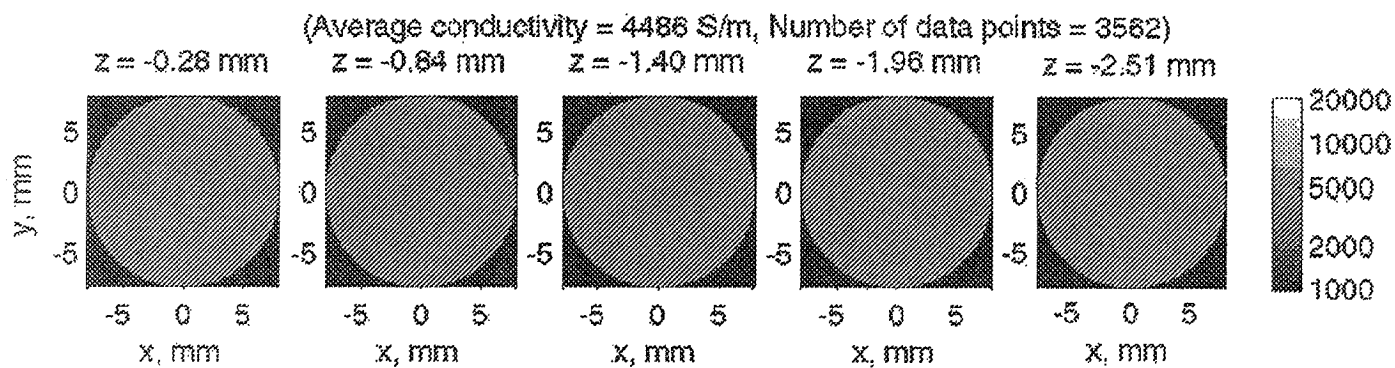


FIG. 6B

**FIG. 7A****FIG. 7B**



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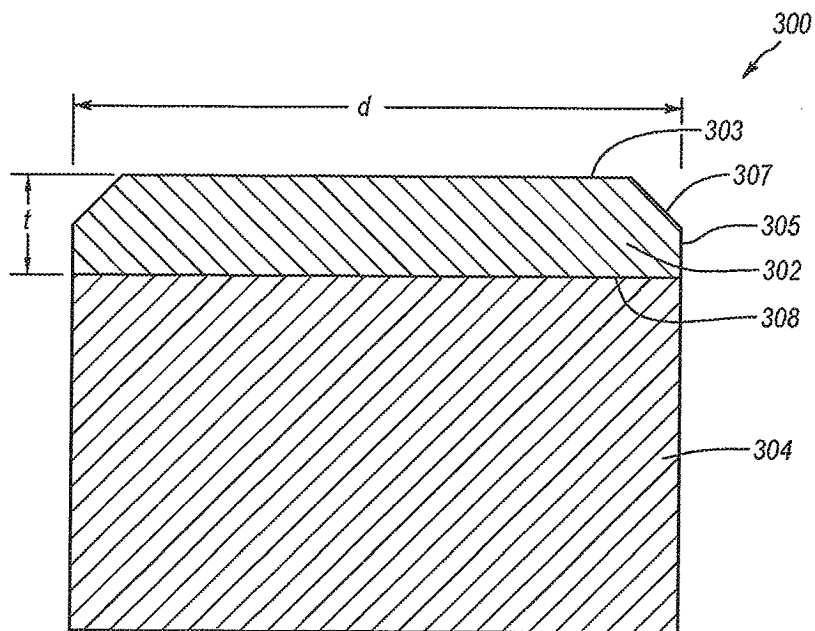


FIG. 8A

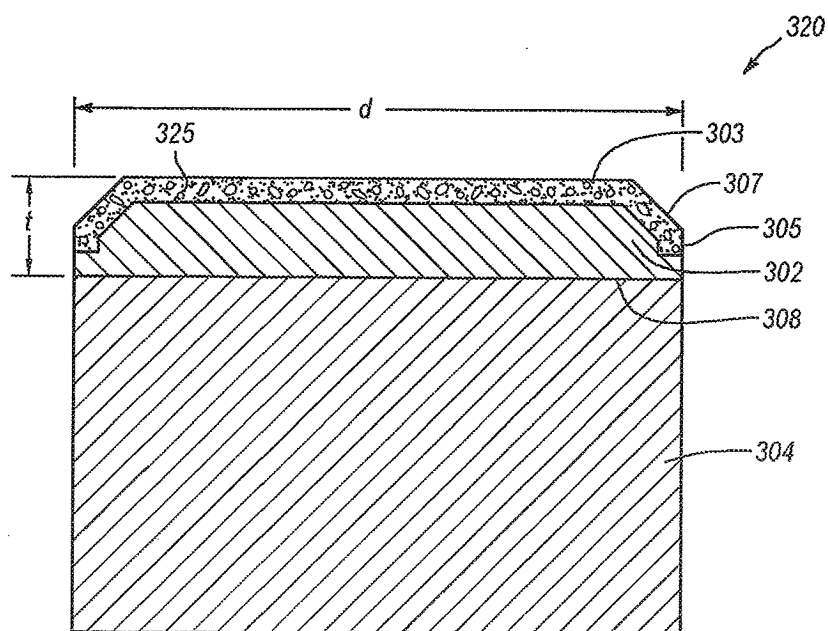


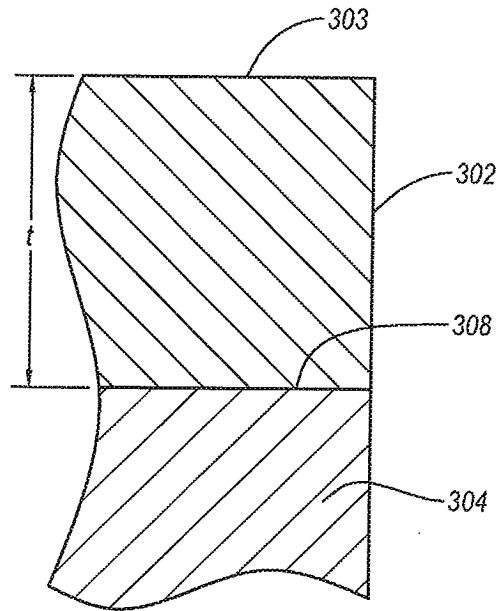
FIG. 8B

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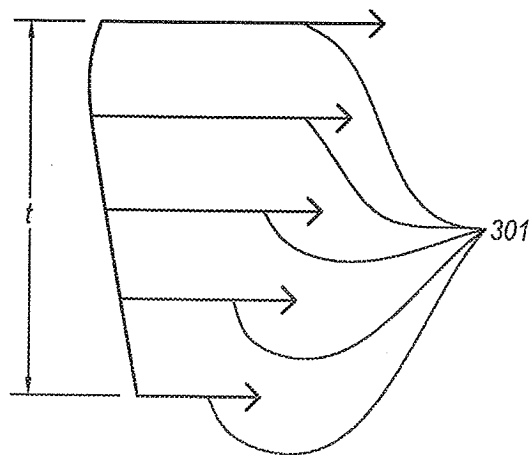
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**FIG. 8C**



**FIG. 8D**

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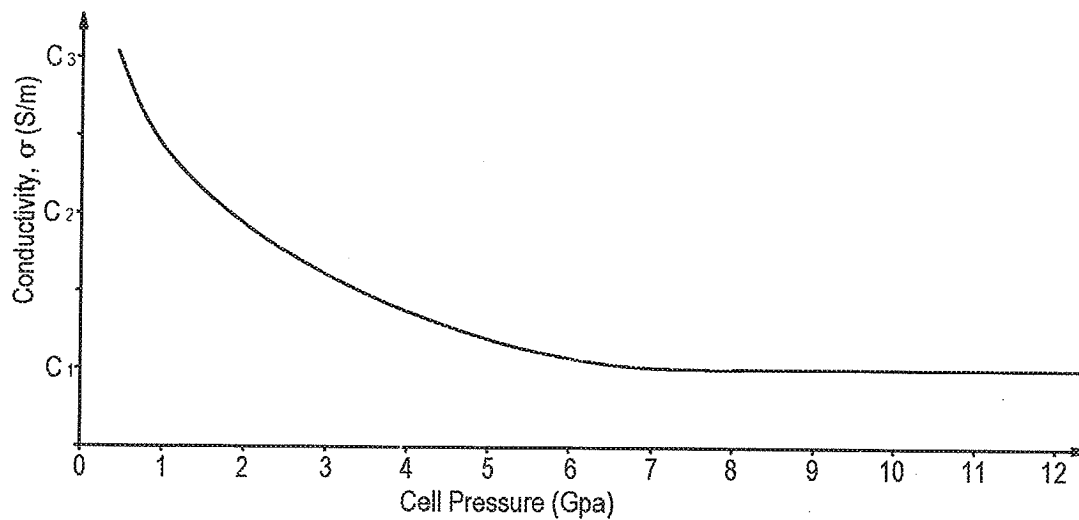


FIG. 9

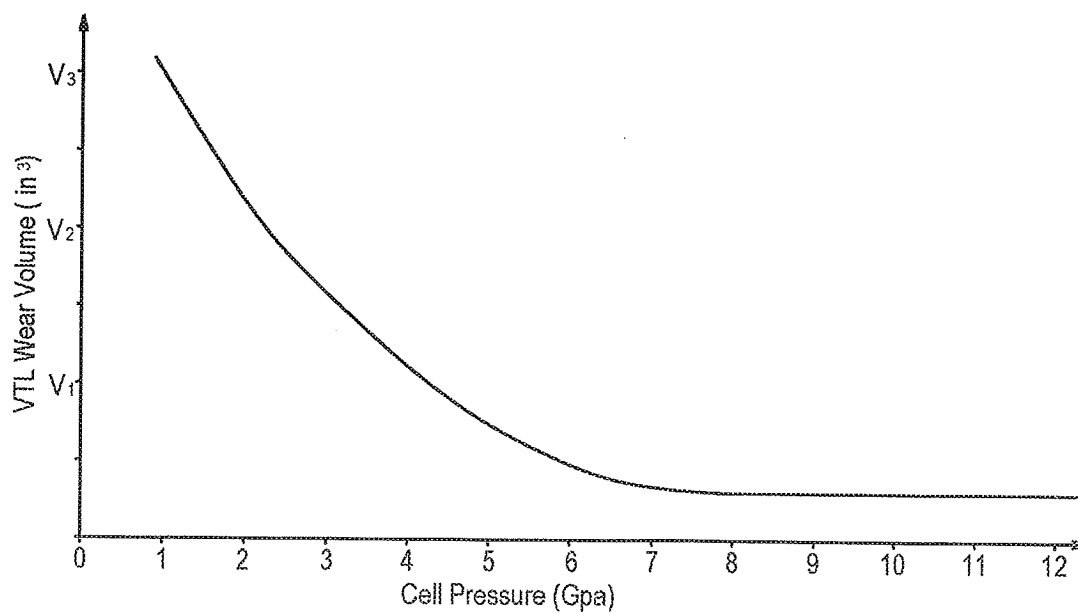


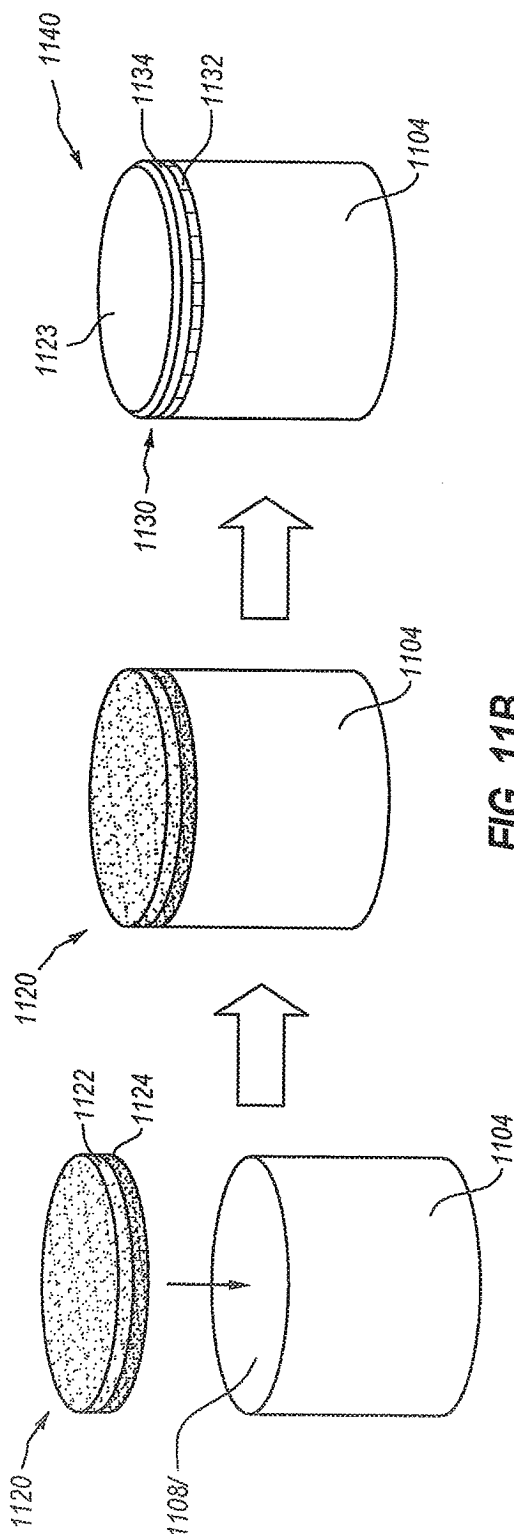
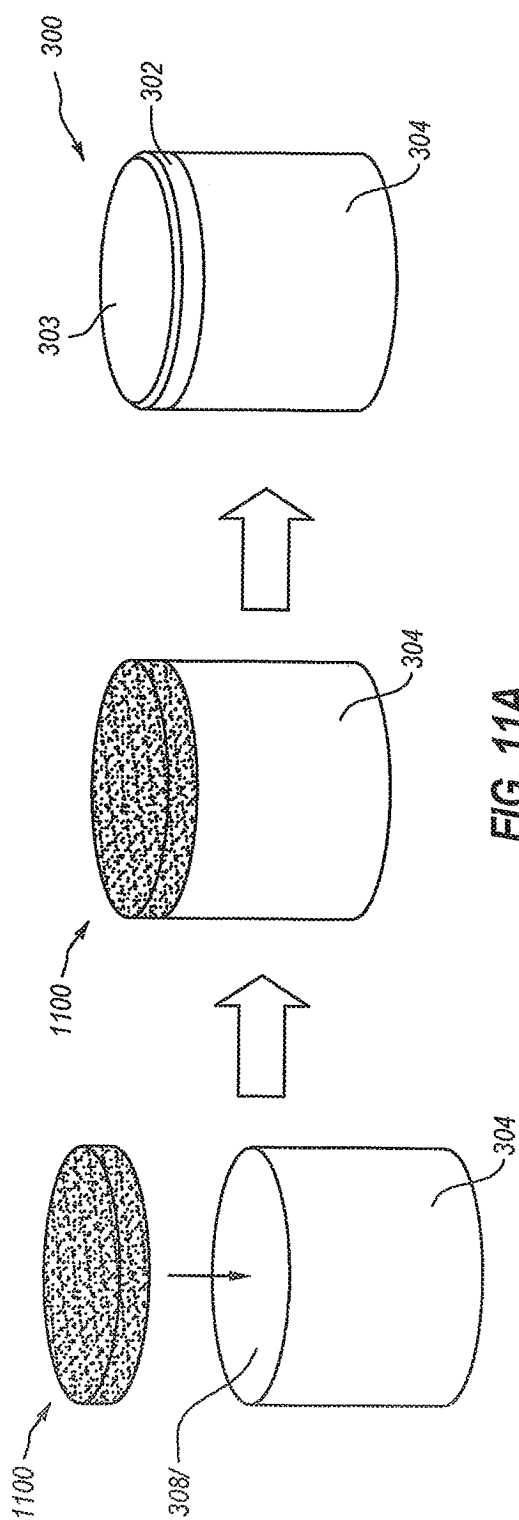
FIG. 10

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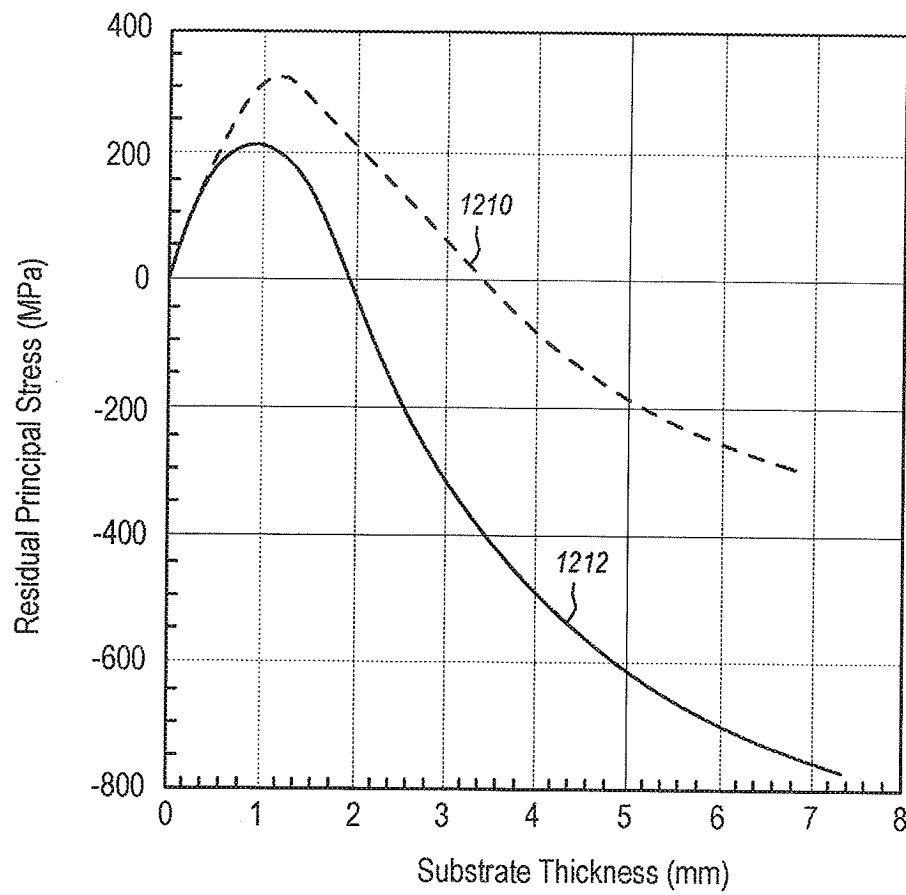


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**FIG. 12**



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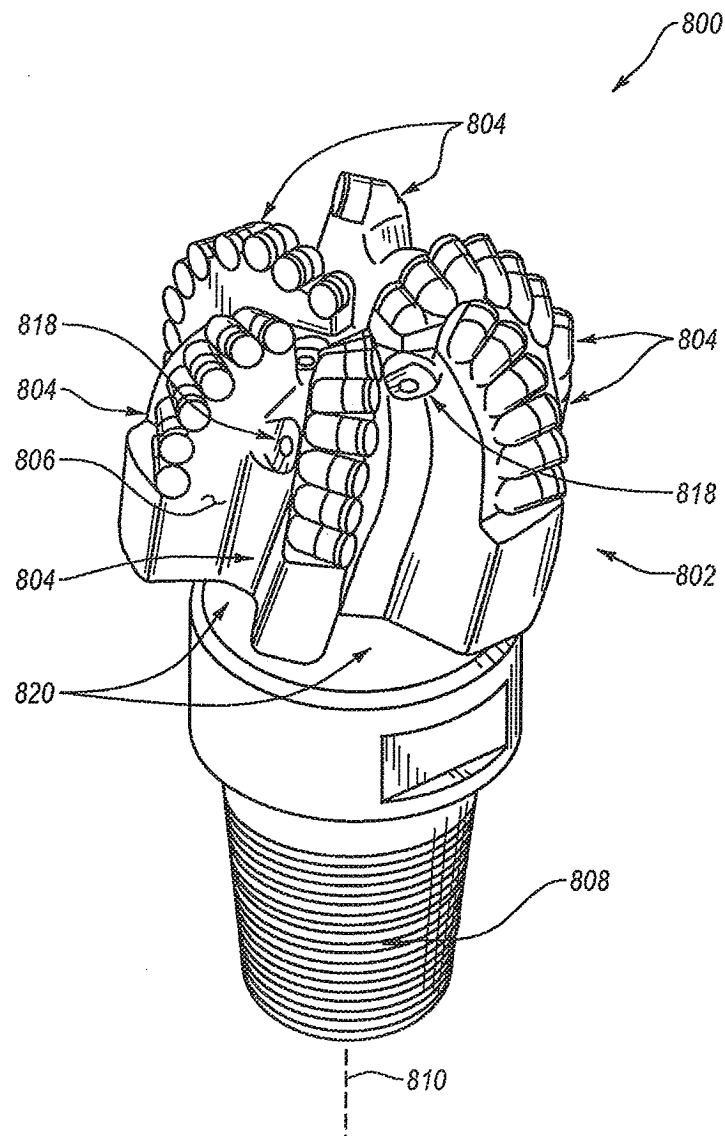


FIG. 13

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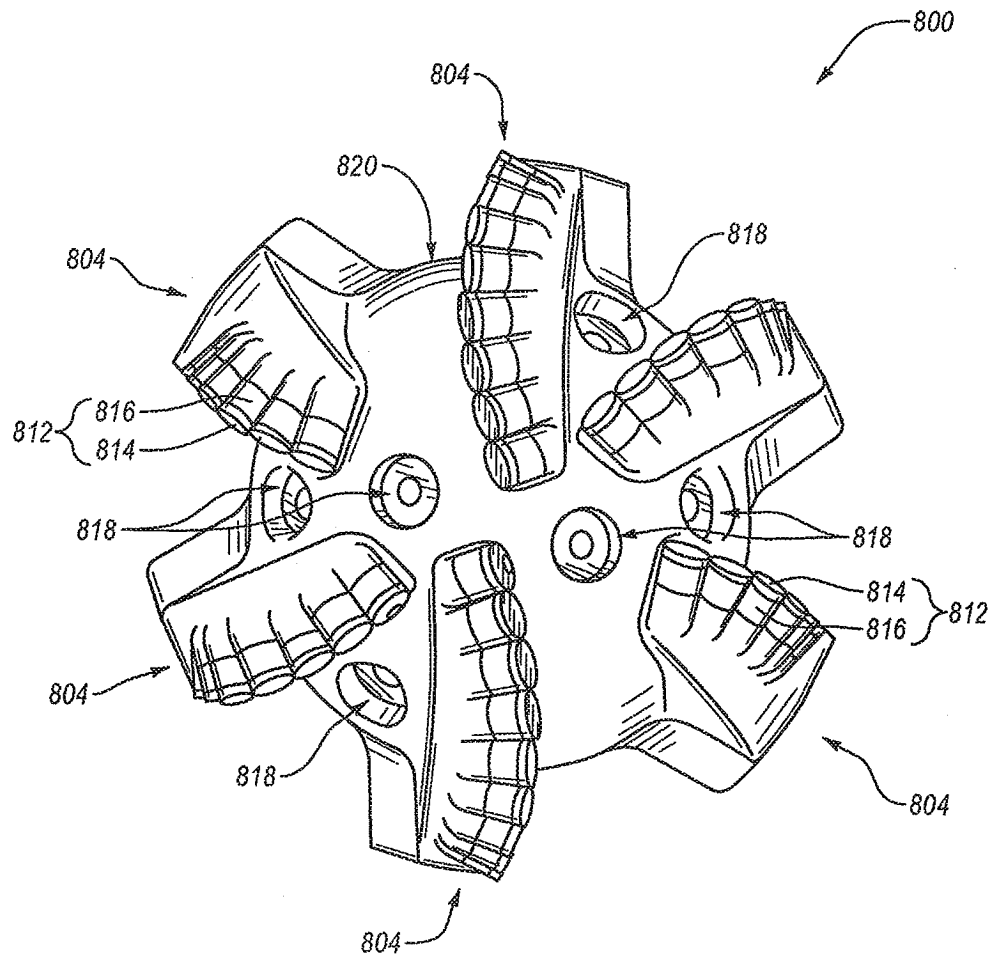


FIG. 14

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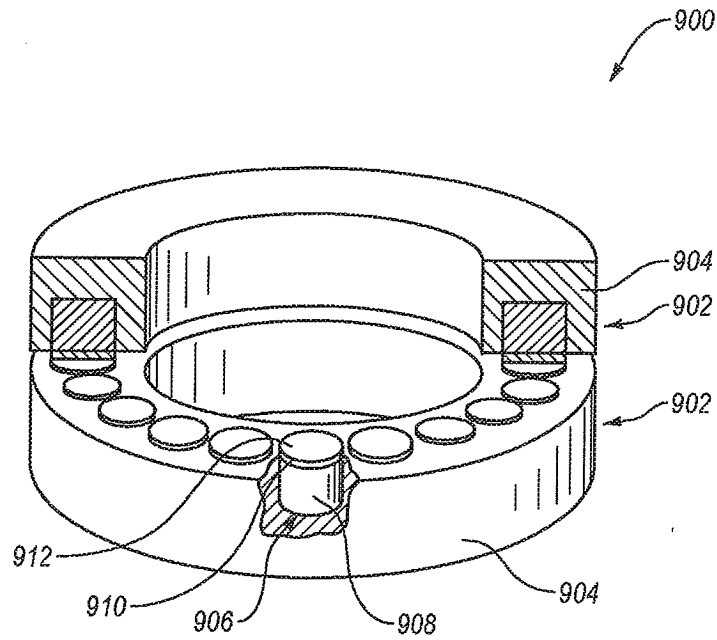


FIG. 15

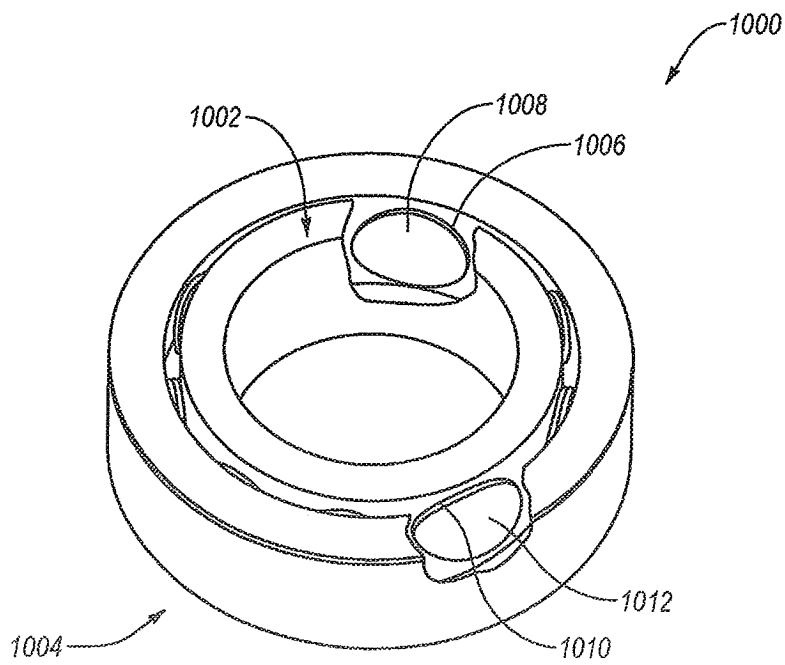


FIG. 16

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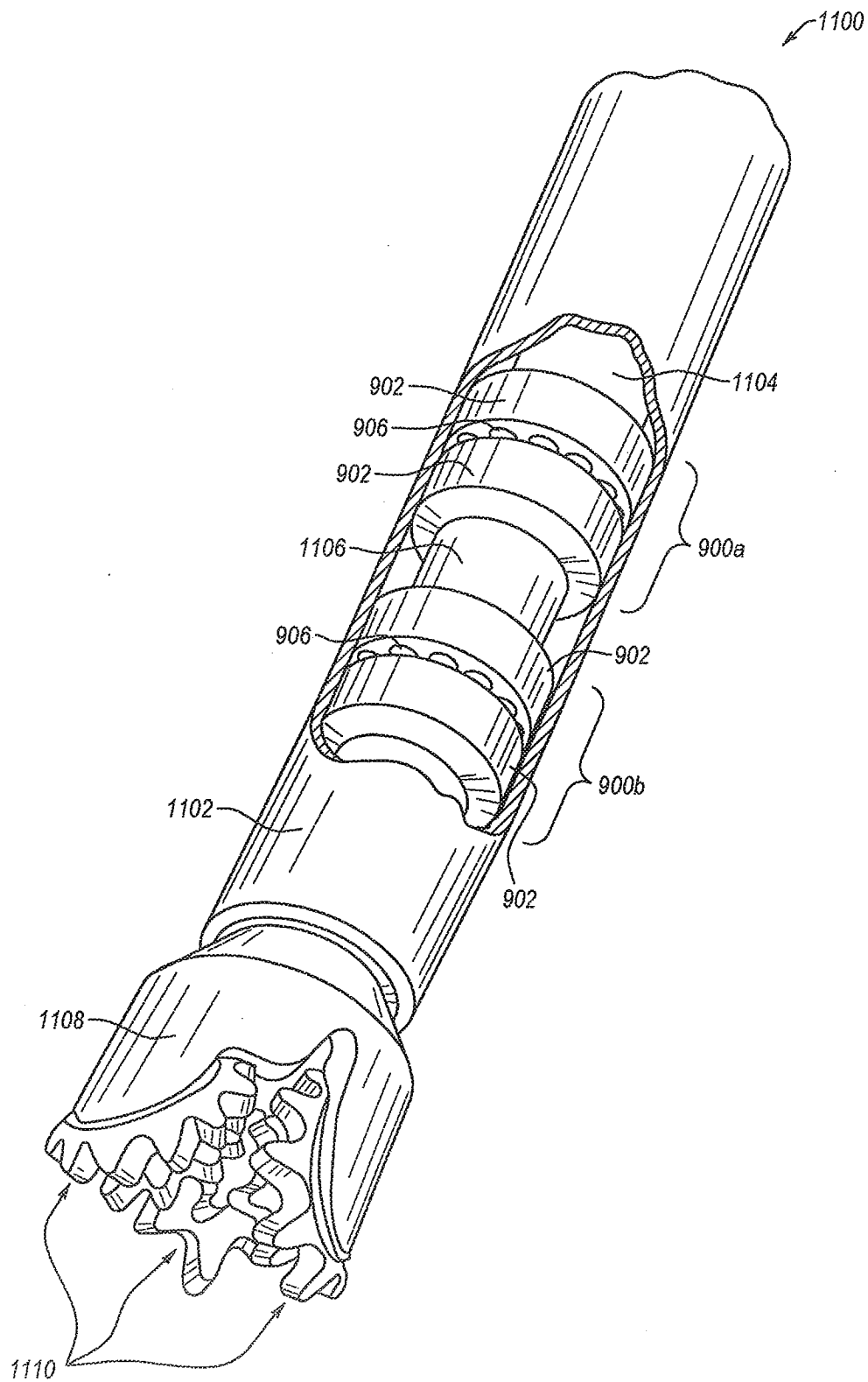


FIG. 17

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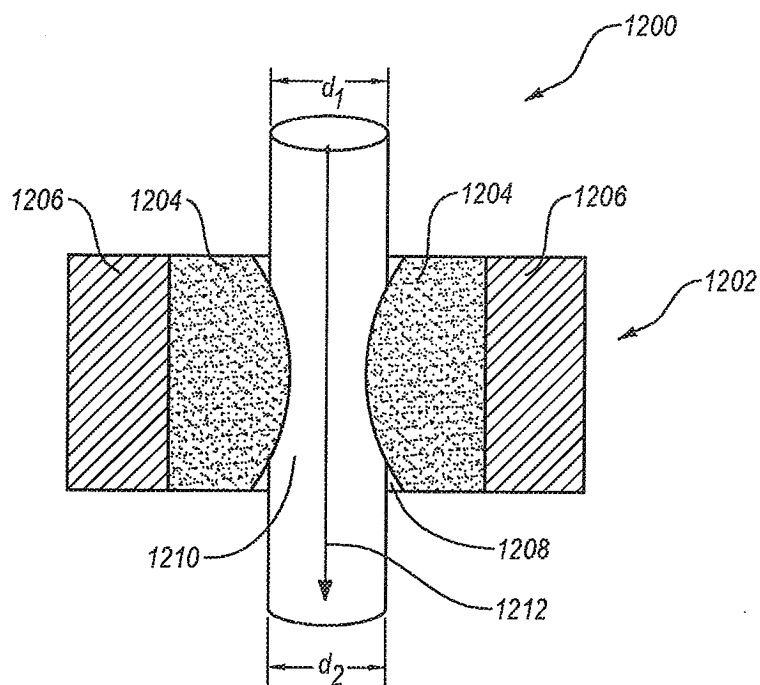


FIG. 18



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**POLYCRYSTALLINE DIAMOND,  
POLYCRYSTALLINE DIAMOND  
COMPACTS, METHODS OF MAKING SAME,  
AND APPLICATIONS**

**CROSS-REFERENCE TO RELATED  
APPLICATIONS**

This application is a continuation of U.S. patent application Ser. No. 13/486,578 filed on 1 Jun. 2012, which is a continuation-in-part of U.S. patent application Ser. No. 12/858,906 filed on 18 Aug. 2010, which is a divisional of U.S. patent application Ser. No. 12/244,960 filed on 3 Oct. 2008 (now U.S. Pat. No. 7,866,418), the contents of each of the foregoing applications are incorporated herein, in their entirety, by this reference.

**BACKGROUND**

Wear-resistant, superabrasive compacts are utilized in a variety of mechanical applications. For example, polycrystalline diamond compacts ("PDCs") are used in drilling tools (e.g., cutting elements, gage trimmers, etc.), machining equipment, bearing apparatuses, wire-drawing machinery, and in other mechanical apparatuses.

PDCs have found particular utility as superabrasive cutting elements in rotary drill bits, such as roller-cone drill bits and fixed-cutter drill bits. A PDC cutting element typically includes a superabrasive diamond layer commonly referred to as a diamond table. The diamond table may be formed and bonded to a substrate using a high-pressure, high-temperature ("HPHT") process. The PDC cutting element may also be brazed directly into a preformed pocket, socket, or other receptacle formed in the bit body. The substrate may often be brazed or otherwise joined to an attachment member, such as a cylindrical backing. A rotary drill bit typically includes a number of PDC cutting elements affixed to the bit body. It is also known that a stud carrying the PDC may be used as a PDC cutting element when mounted to a bit body of a rotary drill bit by press-fitting, brazing, or otherwise securing the stud into a receptacle formed in the bit body.

Conventional PDCs are normally fabricated by placing a cemented carbide substrate into a container with a volume of diamond particles positioned adjacent to the cemented carbide substrate. A number of such cartridges may be loaded into an HPHT press. The substrates and volume of diamond particles are then processed under HPHT conditions in the presence of a catalyst material that causes the diamond particles to bond to one another to form a matrix of bonded diamond grains defining a polycrystalline diamond ("PCD") table that is bonded to the substrate. The catalyst material is often a metal-solvent catalyst (e.g., cobalt, nickel, iron, or alloys thereof) that is used for promoting intergrowth of the diamond particles.

In one conventional approach, a constituent of the cemented carbide substrate, such as cobalt from a cobalt-cemented tungsten carbide substrate, liquefies and sweeps from a region adjacent to the volume of diamond particles into interstitial regions between the diamond particles during the HPHT process. The cobalt acts as a catalyst to promote intergrowth between the diamond particles, which results in formation of bonded diamond grains. Often, a solvent catalyst may be mixed with the diamond particles prior to subjecting the diamond particles and substrate to the HPHT process.

The presence of the solvent catalyst in the PCD table is believed to reduce the thermal stability of the PCD table at

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elevated temperatures. For example, the difference in thermal expansion coefficient between the diamond grains and the solvent catalyst is believed to lead to chipping or cracking of the PCD table during drilling or cutting operations, which can degrade the mechanical properties of the PCD table or cause failure. Additionally, some of the diamond grains can undergo a chemical breakdown or back-conversion to graphite via interaction with the solvent catalyst. At elevated high temperatures, portions of the diamond grains may transform to carbon monoxide, carbon dioxide, graphite, or combinations thereof, thus degrading the mechanical properties of the PDC.

One conventional approach for improving the thermal stability of a PDC is to at least partially remove the solvent catalyst from the PCD table of the PDC by acid leaching. However, removing the solvent catalyst from the PCD table can be relatively time consuming for high-volume manufacturing. Additionally, depleting the solvent catalyst may decrease the mechanical strength of the PCD table.

Despite the availability of a number of different PCD materials, manufacturers and users of PCD materials continue to seek PCD materials that exhibit improved mechanical and/or thermal properties.

**SUMMARY**

Embodiments of the invention relate to PCD exhibiting enhanced diamond-to-diamond bonding and related PDCs, rotary drill bits, and methods of fabrication. In an embodiment, PCD includes a plurality of diamond grains defining a plurality of interstitial regions. The plurality of diamond grains exhibit an average grain size of about 30  $\mu\text{m}$  or less. A metal-solvent catalyst occupies at least a portion of the plurality of interstitial regions. The plurality of diamond grains and the metal-solvent catalyst collectively may exhibit an average electrical conductivity of less than about 1200 S/m.

In an embodiment, a PDC includes a PCD table having a plurality of diamond grains defining a plurality of interstitial regions. The PCD table is bonded to a substrate. A metal-solvent catalyst occupies at least a portion of the plurality of interstitial regions. The plurality of diamond grains exhibit an average grain size of about 30  $\mu\text{m}$  or less. The plurality of diamond grains and the metal-solvent catalyst collectively may exhibit an average electrical conductivity of less than about 1200 S/m.

In an embodiment, a method includes enclosing a plurality of diamond particles and a metal-solvent catalyst in a pressure transmitting medium to form a cell assembly. The plurality of the diamond particles exhibits an average particle size of about 30  $\mu\text{m}$  or less. The method further includes subjecting the cell assembly to a temperature of at least about 1000° Celsius and a pressure in the pressure transmitting medium of at least about 7.5 GPa to form PCD. The PCD exhibits an average electrical conductivity of less than about 1200 S/m.

In an embodiment a rotary drill bit includes a bit body including a leading end structure configured to facilitate drilling a subterranean formation. The rotary drill bit also includes a plurality of cutting elements mounted to the blades. At least one of the plurality of cutting elements includes a PCD element. At least a portion of the PCD element includes a plurality of diamond grains defining a plurality of interstitial regions, the plurality of interstitial regions, including metal-solvent catalyst. The at least a portion of the PCD element exhibits an average electrical conductivity of less than about 1200 S/m.

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Further embodiments relate to applications utilizing the disclosed PCD and PDCs in various articles and apparatuses, such as rotary drill bits, bearing apparatuses, wire-drawing dies, machining equipment, and other articles and apparatuses.

Features from any of the disclosed embodiments may be used in combination with one another, without limitation. In addition, other features and advantages of the present disclosure will become apparent to those of ordinary skill in the art through consideration of the following detailed description and the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The drawings illustrate several embodiments of the invention, wherein identical reference numerals refer to identical elements or features in different views or embodiments shown in the drawings.

FIG. 1A is a schematic diagram of an example of a magnetic saturation apparatus configured to magnetize a PCD sample approximately to saturation.

FIG. 1B is a schematic diagram of an example of a magnetic saturation measurement apparatus configured to measure a saturation magnetization of a PCD sample.

FIG. 2 is a schematic diagram of an example of a coercivity measurement apparatus configured to determine a coercivity of a PCD sample.

FIG. 3A is an isometric view of an embodiment of a PCD including a PCD table formed from any of the PCD embodiments disclosed herein.

FIG. 3B is a functional block diagram of an embodiment of a multi-probe resistance measurement testing system configured to measure electrical resistance of a PCD table that may be used to measure electrical conductivity of the PCD or PCD tables disclosed herein.

FIG. 4 is a schematic diagram for four-probe electrical resistance measurements on a PDC sample using the system shown in FIG. 3A.

FIG. 5 is a top isometric view of the sensor-probe arrangement of the testing system shown in FIG. 4.

FIG. 6A is an isometric view of an embodiment of a sample-holder assembly for holding a PDC sample to be tested.

FIG. 6B is a cross-sectional view of the sample-holder assembly shown in FIG. 6A, with a PDC sample to be tested held therein.

FIGS. 7A and 7B are electrical conductivity distributions in PCD tables of two different PDC cutter samples, with the electrical conductivity grey scale in Siemens/meter ("S/m").

FIG. 8A is a cross-sectional view of an embodiment of a PDC including a PCD table formed from any of the PCD embodiments disclosed herein.

FIG. 8B is a cross-sectional view of an embodiment of a PDC illustrating a PCD table that has been leached to deplete metal-solvent catalyst from a region thereof.

FIG. 8C is an enlarged cross-sectional view of FIG. 8A of the PDC shown in FIG. 8A.

FIG. 8D is an electrical conductivity gradient profile of the PCD table shown in FIG. 8A showing the magnitude of the electrical conductivity represented as arrow length, with the magnitude of the electrical conductivity decreasing with distance from the working surface.

FIG. 9 is a graph illustrating the electrical conductivity,  $\sigma$ , versus cell pressure relationship in which electrical conductivity decreases with increasing cell pressure.

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FIG. 10 is a graph illustrating the wear volume from a vertical turret lathe ("VTL") test versus cell pressure relationship in which wear volume decreases with increasing cell pressure.

FIG. 11A is a schematic illustration of a method of fabricating the PDC shown in FIG. 8A.

FIG. 11B is a schematic illustration of a method of fabricating another embodiment of a PDC using the methods disclosed herein.

FIG. 12 is a graph illustrating residual principal stress versus substrate thickness that was measured in a PCD table of a PDC fabricated at a pressure above about 7.5 GPa and a PCD table of a conventionally formed PDC.

FIG. 13 is an isometric view of an embodiment of a rotary drill bit that may employ one or more of the disclosed PDC embodiments.

FIG. 14 is a top elevation view of the rotary drill bit shown in FIG. 13.

FIG. 15 is an isometric cut-away view of an embodiment of a thrust-bearing apparatus that may utilize one or more of the disclosed PDC embodiments.

FIG. 16 is an isometric cut-away view of an embodiment of a radial bearing apparatus that may utilize one or more of the disclosed PDC embodiments.

FIG. 17 is a schematic isometric cut-away view of an embodiment of a subterranean drilling system including the thrust-bearing apparatus shown in FIG. 15.

FIG. 18 is a side cross-sectional view of an embodiment of a wire-drawing die that employs a PDC fabricated in accordance with the principles described herein.

#### DETAILED DESCRIPTION

Embodiments of the invention relate to PCD exhibiting enhanced diamond-to-diamond bonding and related PDCs, rotary drill bits, and methods of fabrication. It is currently believed by the inventors that as the sintering cell pressure employed during the HPHT process used to fabricate such PCD is moved further into the diamond-stable region away from the graphite-diamond equilibrium line, the rate of nucleation and growth of diamond increases. Such increased nucleation and growth of diamond between diamond particles (for a given diamond particle formulation) may result in PCD being formed exhibiting a relatively lower metal-solvent catalyst content with an associated relatively low average electrical conductivity, a higher coercivity, a lower specific magnetic saturation, and/or a lower specific permeability (i.e., the ratio of specific magnetic saturation to coercivity) than PCD formed at a lower sintering pressure. Embodiments also relate to PDCs having a PCD table comprising such PCD, methods of fabricating such PCD and PDCs, and applications for such PCD and PDCs in rotary drill bits, bearing apparatuses, wire-drawing dies, machining equipment, and other articles and apparatuses.

#### PCD Embodiments

According to various embodiments, unleached PCD sintered at a pressure of at least about 7.5 GPa may exhibit a coercivity of 115 Oe or more, a high-degree of diamond-to-diamond bonding, a specific magnetic saturation of about 15 G-cm<sup>3</sup>/g or less, a metal-solvent catalyst content of about 7.5 weight % ("wt %") or less, an electrical conductivity of less than about 1200 S/m, or combinations thereof. The PCD includes a plurality of diamond grains directly bonded together via diamond-to-diamond bonding to define a plurality of interstitial regions. At least a portion of the inter-

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stitial regions or, in some embodiments, substantially all, or a substantial portion of the interstitial regions may be occupied by a metal-solvent catalyst, such as iron, nickel, cobalt, or alloys of any of the foregoing metals. For example, the metal-solvent catalyst may be a cobalt-based material including at least 50 wt % cobalt, such as a cobalt alloy.

The diamond grains may exhibit an average grain size of about 50  $\mu\text{m}$  or less, such as about 30  $\mu\text{m}$  or less or about 20  $\mu\text{m}$  or less. For example, the average grain size of the diamond grains may be about 10  $\mu\text{m}$  to about 20  $\mu\text{m}$ , about 15  $\mu\text{m}$  to about 19.5  $\mu\text{m}$ , about 15  $\mu\text{m}$  to about 18  $\mu\text{m}$ , about 10  $\mu\text{m}$  to about 18  $\mu\text{m}$ , or about 5  $\mu\text{m}$  to about 18  $\mu\text{m}$ . In some embodiments, the average grain size of the diamond grains may be about 10  $\mu\text{m}$  or less, such as about 2  $\mu\text{m}$  to about 5  $\mu\text{m}$  or submicron. The diamond grain size distribution of the diamond grains may exhibit a single mode, or may be a bimodal or greater grain size distribution.

The metal-solvent catalyst that occupies the interstitial regions may be present in the PCD in an amount of about 7.5 wt % or less. In some embodiments, the metal-solvent catalyst may be present in the PCD in an amount of greater than 0 wt % to about 7.5 wt %, about 3 wt % to about 7.5 wt %, greater than 0 wt % to about 6 wt %, or about 3 wt % to about 6 wt %. In other embodiments, the metal-solvent catalyst content may be present in the PCD in an amount less than about 3 wt %, such as about 1 wt % to about 3 wt % or a residual amount to about 1 wt %. By maintaining the metal-solvent catalyst content below about 7.5 wt %, the PCD may exhibit a desirable level of thermal stability suitable for subterranean drilling applications.

Many physical characteristics of the PCD may be determined by measuring certain magnetic and electrical properties of the PCD because the metal-solvent catalyst may be ferromagnetic. The amount of the metal-solvent catalyst present in the PCD may be correlated with the measured specific magnetic saturation of the PCD. A relatively larger specific magnetic saturation indicates relatively more metal-solvent catalyst in the PCD.

The mean free path between neighboring diamond grains of the PCD may be correlated with the measured coercivity of the PCD. A relatively large coercivity indicates a relatively smaller mean free path. The mean free path is representative of the average distance between neighboring diamond grains of the PCD, and thus may be indicative of the extent of diamond-to-diamond bonding in the PCD. A relatively smaller mean free path, in well-sintered PCD, may indicate relatively more diamond-to-diamond bonding.

As merely one example, ASTM B886-03 (2008) provides a suitable standard for measuring the specific magnetic saturation and ASTM B887-03 (2008) e1 provides a suitable standard for measuring the coercivity of the PCD. Although both ASTM B886-03 (2008) and ASTM B887-03 (2008) e1 are directed to standards for measuring magnetic properties of cemented carbide materials, either standard may be used to determine the magnetic properties of PCD. A KOERZIMAT CS 1.096 instrument (commercially available from Foerster Instruments of Pittsburgh, Pa.) is one suitable instrument that may be used to measure the specific magnetic saturation and the coercivity of the PCD.

Generally, as the sintering pressure that is used to form the PCD increases, the coercivity may increase while the magnetic saturation and electrical conductivity may decrease. The PCD defined collectively by the bonded diamond grains and the metal-solvent catalyst may exhibit one or more of the following properties: a coercivity of about 115 Oe or more, a metal-solvent catalyst content of less than about 7.5

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wt % as indicated by a specific magnetic saturation of about 15  $\text{G}\cdot\text{cm}^3/\text{g}$  or less, or an electrical conductivity less than about 1200 S/m. For example, the electrical conductivity may be an average electrical conductivity of the PCD (e.g., a PCD table) or a region of the PCD. In a more detailed embodiment, the coercivity of the PCD may be about 115 Oe to about 250 Oe, the specific magnetic saturation of the PCD may be greater than 0  $\text{G}\cdot\text{cm}^3/\text{g}$  to about 15  $\text{G}\cdot\text{cm}^3/\text{g}$ , and the electrical conductivity may be about 25 S/m to about 1000 S/m. In an even more detailed embodiment, the coercivity of the PCD may be about 115 Oe to about 175 Oe, the specific magnetic saturation of the PCD may be about 5  $\text{G}\cdot\text{cm}^3/\text{g}$  to about 15  $\text{G}\cdot\text{cm}^3/\text{g}$ , and the electrical conductivity may be less than about 750 S/m. In another more detailed embodiment, the coercivity of the PCD may be about 155 Oe to about 175 Oe, the specific magnetic saturation of the PCD may be about 10  $\text{G}\cdot\text{cm}^3/\text{g}$  to about 15  $\text{G}\cdot\text{cm}^3/\text{g}$ , and the electrical conductivity may be less than about 500 S/m. In yet another embodiment the coercivity of the PCD may be 155 Oe to about 175 Oe, the specific magnetic saturation of the PCD may be about 10  $\text{G}\cdot\text{cm}^3/\text{g}$  to about 15  $\text{G}\cdot\text{cm}^3/\text{g}$ , and the electrical conductivity may be about 100 S/m to about 500 S/m. In another embodiment, the coercivity of the PCD may be about 130 Oe to about 160 Oe, the specific magnetic saturation of the PCD may be about 5  $\text{G}\cdot\text{cm}^3/\text{g}$  to about 15  $\text{G}\cdot\text{cm}^3/\text{g}$ , and the electrical conductivity may be about 50 S/m to about 150 S/m. The specific permeability (i.e., the ratio of specific magnetic saturation to coercivity) of the PCD may be about 0.10 or less, such as about 0.060 to about 0.090. Despite the average grain size of the bonded diamond grains being less than about 30  $\mu\text{m}$ , the metal-solvent catalyst content in the PCD may be less than about 7.5 wt % resulting in a desirable thermal stability.

As discussed above, the electrical conductivity of the PCD may be less than 1200 S/m. In some embodiments, the electrical conductivity may be less than 1000 S/m, such as about 25 S/m to about 1000 S/m. In other embodiments, the electrical conductivity may be less than 750 S/m. In another embodiment, the electrical conductivity may be less than 500 S/m, such as about 100 S/m to about 500 S/m. In a more restrictive embodiment, the electrical conductivity may be about 50 S/m to about 150 S/m.

In an embodiment, diamond particles having an average particle size of about 18  $\mu\text{m}$  to about 20  $\mu\text{m}$  are positioned adjacent to a cobalt-cemented tungsten carbide substrate and subjected to an HPHT process at a temperature of about 1390° C. to about 1430° C. and a pressure of about 7.8 GPa to about 8.5 GPa. The PCD so-formed as a PCD table bonded to the substrate may exhibit one or more of the following properties: a coercivity of about 155 Oe to about 175 Oe, a specific magnetic saturation of about 10  $\text{G}\cdot\text{cm}^3/\text{g}$  to about 15  $\text{G}\cdot\text{cm}^3/\text{g}$ , and a cobalt content of about 5 wt % to about 7.5 wt %, or an electrical conductivity less than about 750 S/m.

In one or more embodiments, a specific magnetic saturation constant for the metal-solvent catalyst in the PCD may be about 185  $\text{G}\cdot\text{cm}^3/\text{g}$  to about 215  $\text{G}\cdot\text{cm}^3/\text{g}$ . For example, the specific magnetic saturation constant for the metal-solvent catalyst in the PCD may be about 195  $\text{G}\cdot\text{cm}^3/\text{g}$  to about 205  $\text{G}\cdot\text{cm}^3/\text{g}$ . It is noted that the specific magnetic saturation constant for the metal-solvent catalyst in the PCD may be composition dependent.

Generally, as the sintering pressure is increased above 7.5 GPa, a wear resistance of the PCD so-formed may increase relative to PCD formed at lower pressures. For example, the  $G_{ratio}$  may be at least about  $4.0 \times 10^6$ , such as about  $5.0 \times 10^6$  to about  $15.0 \times 10^6$  or, more particularly, about  $8.0 \times 10^6$  to



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about  $15.0 \times 10^6$ . In some embodiments, the  $G_{ratio}$  may be at least about  $30.0 \times 10^6$ . The  $G_{ratio}$  is the ratio of the volume of workpiece cut to the volume of PCD worn away during a cutting process, such as in a vertical turret lathe ("VTL") test in which the workpiece is cooled during the cutting process. An example of suitable parameters that may be used to determine a  $G_{ratio}$  of the PCD are a depth of cut for the PCD cutting element of about 0.254 mm, a back rake angle for the PCD cutting element of about 20 degrees, an in-feed for the PCD cutting element of about 6.35 mm/rev, a rotary speed of the workpiece to be cut of about 101 rpm, and the workpiece may be made from Barre granite having a 914 mm outer diameter and a 254 mm inner diameter. During the  $G_{ratio}$  test, the workpiece is cooled with a coolant, such as water.

In addition to the aforementioned  $G_{ratio}$ , despite the presence of the metal-solvent catalyst in the PCD, the PCD may exhibit a thermal stability that is close to, substantially the same as, or greater than a partially leached PCD material formed by sintering a substantially similar diamond particle formulation at a lower sintering pressure (e.g., up to about 5.5 GPa) and in which the metal-solvent catalyst (e.g., cobalt) is leached therefrom to a depth of about 60  $\mu$ m to about 100  $\mu$ m from a working surface. The thermal stability of the PCD may be evaluated by measuring the distance cut in a workpiece prior to catastrophic failure, without using coolant, in a vertical lathe test (e.g., vertical turret lathe or a vertical boring mill). An example of suitable parameters that may be used to determine thermal stability of the PCD are a depth of cut for the PCD cutting element of about 1.27 mm, a back rake angle for the PCD cutting element of about 20 degrees, an in-feed for the PCD cutting element of about 1.524 mm/rev, a cutting speed of the workpiece to be cut of about 1.78 m/sec, and the workpiece may be made from Barre granite having a 914 mm outer diameter and a 254 mm inner diameter. In an embodiment, the distance cut in a workpiece prior to catastrophic failure as measured in the above-described vertical lathe test may be at least about 1300 m, such as about 1300 m to about 3950 m.

PCD formed by sintering diamond particles having the same diamond particle size distribution as a PCD embodiment of the invention, but sintered at a pressure of, for example, up to about 5.5 GPa and at temperatures in which diamond is stable may exhibit a coercivity of about 100 Oe or less, a specific magnetic saturation of about 16 G-cm<sup>3</sup>/g or more, and an electrical conductivity of about 750 S/m or more. Thus, in one or more embodiments of the invention, PCD exhibits a metal-solvent catalyst content of less than 7.5 wt % and a greater amount of diamond-to-diamond bonding between diamond grains than that of a PCD sintered at a lower pressure, but with the same precursor diamond particle size distribution and catalyst.

It is currently believed by the inventors that forming the PCD by sintering diamond particles at a pressure of at least about 7.5 GPa may promote nucleation and growth of diamond between the diamond particles being sintered so that the volume of the interstitial regions of the PCD so-formed is decreased compared to the volume of interstitial regions if the same diamond particle distribution was sintered at a pressure of, for example, up to about 5.5 GPa and at temperatures where diamond is stable. For example, the diamond may nucleate and grow from carbon provided by dissolved carbon in metal-solvent catalyst (e.g., liquefied cobalt) infiltrating into the diamond particles being sintered, partially graphitized diamond particles, carbon from a substrate, carbon from another source (e.g., graphite particles and/or fullerenes mixed with the diamond particles), or

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combinations of the foregoing. This nucleation and growth of diamond in combination with the sintering pressure of at least about 7.5 GPa may contribute to PCD so-formed having a metal-solvent catalyst content of less than about 7.5 wt %.

FIGS. 1A, 1B, and 2 schematically illustrate the manner in which the specific magnetic saturation and the coercivity of the PCD may be determined using an apparatus, such as the KOERZIMAT CS 1.096 instrument. FIG. 1A is a schematic diagram of an example of a magnetic saturation apparatus 100 configured to magnetize a PCD sample to saturation. The magnetic saturation apparatus 100 includes a saturation magnet 102 of sufficient strength to magnetize a PCD sample 104 at least approximately to saturation. The saturation magnet 102 may be a permanent magnet or an electromagnet. In the illustrated embodiment, the saturation magnet 102 is a permanent magnet that defines an air gap 106, and the PCD sample 104 may be positioned on a sample holder 108 within the air gap 106. When the PCD sample 104 is light-weight, it may be secured to the sample holder 108 using, for example, double-sided tape or other adhesive so that the PCD sample 104 does not move responsive to the magnetic field from the saturation magnet 102 and the PCD sample 104 is magnetized approximately to saturation.

Referring to the schematic diagram of FIG. 1B, after magnetizing the PCD sample 104 approximately to saturation using the magnetic saturation apparatus 100, a magnetic saturation of the PCD sample 104 may be measured using a magnetic saturation measurement apparatus 120. The magnetic saturation measurement apparatus 120 includes a Helmholtz measuring coil 122 defining a passageway dimensioned so that the magnetized PCD sample 104 may be positioned therein on a sample holder 124. Once positioned in the passageway, the sample holder 124 supporting the magnetized PCD sample 104 may be moved axially along an axis direction 126 to induce a current in the Helmholtz measuring coil 122. Measurement electronics 128 are coupled to the Helmholtz measuring coil 122 and configured to calculate the magnetic saturation based upon the measured current passing through the Helmholtz measuring coil 122. The measurement electronics 128 may also be configured to calculate a weight percentage of magnetic material in the PCD sample 104 when the composition and magnetic characteristics of the metal-solvent catalyst in the PCD sample 104 are known, such as with iron, nickel, cobalt, and alloys thereof. Specific magnetic saturation may be calculated based upon the calculated magnetic saturation and the measured weight of the PCD sample 104.

The amount of metal-solvent catalyst in the PCD sample 104 may be determined using a number of different analytical techniques. For example, energy dispersive spectroscopy (e.g., EDAX), wavelength dispersive x-ray spectroscopy (e.g., WDX), and/or Rutherford backscattering spectroscopy may be employed to determine the amount of metal-solvent catalyst in the PCD sample 104.

If desired, a specific magnetic saturation constant of the metal-solvent catalyst content in the PCD sample 104 may be determined using an iterative approach. A value for the specific magnetic saturation constant of the metal-solvent catalyst in the PCD sample 104 may be iteratively chosen until a metal-solvent catalyst content calculated by the analysis software of the KOERZIMAT CS 1.096 instrument using the chosen value substantially matches the metal-solvent catalyst content determined via an analytical technique, such as energy dispersive spectroscopy, wavelength dispersive x-ray spectroscopy, and/or Rutherford backscattering spectroscopy.

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FIG. 2 is a schematic diagram of a coercivity measurement apparatus 200 configured to determine a coercivity of a PCD sample. The coercivity measurement apparatus 200 includes a coil 202 and measurement electronics 204 coupled to the coil 202. The measurement electronics 204 are configured to pass a current through the coil 202 so that a magnetic field is generated. A sample holder 206 having a PCD sample 208 thereon may be positioned within the coil 202. A magnetization sensor 210 configured to measure a magnetization of the PCD sample 208 may be coupled to the measurement electronics 204 and positioned in proximity to the PCD sample 208.

During testing, the magnetic field generated by the coil 202 magnetizes the PCD sample 208 approximately to saturation. Then, the measurement electronics 204 apply a current so that the magnetic field generated by the coil 202 is increasingly reversed. The magnetization sensor 210 measures a magnetization of the PCD sample 208 resulting from application of the reversed magnetic field to the PCD sample 208. The measurement electronics 204 determine the coercivity of the PCD sample 208, which is a measurement of the reverse magnetic field at which the magnetization of the PCD sample 208 is zero.

Although diamond is not electrically conductive by itself, the sintering process for fabricating PCD introduces small amounts of metal-solvent catalyst (e.g., iron, nickel, cobalt, or alloys thereof) into the interstitial regions between the bonded diamond grains of the PCD. For example, cobalt present during sintering of diamond particles, may act as a metal-solvent catalyst that promotes diamond-to-diamond crystal bonding between the diamond grains during the HPHT sintering process. The macroscopic electrical conductivity of PCD may be related to the metal-solvent catalyst content therein.

Additives to the PCD table may also influence the electrical conductivity thereof. For example, the PCD table may include silicon, silicon carbide, graphite, tungsten, tungsten carbide, boron, combinations thereof, or other selected constituents. Some additives may be alloyed with the metal-solvent catalyst of the PCD table (prior to or during the HPHT process) that is present interstitially between bonded diamond grains. For example, cobalt may be alloyed with tungsten and/or boron.

An embodiment of a PDC 300 including a PCD table 302 and a cemented carbide substrate 304 is shown in FIG. 3A. The PCD table 302 includes at least one lateral surface 305, an upper exterior working surface 303, and may include an optional chamfer 307 formed therebetween. It is noted that at least a portion of the at least one lateral surface 305 and/or the chamfer 307 may also function as a working surface (e.g., that contacts a subterranean formation during drilling operations).

An average electrical conductivity for the PCD table 302 may be calculated based at least partially on at least one measured electrical resistance. Because measurements may be taken at a plurality of locations, any non-uniformity within the distribution of the electrical conductivity of the PCD table 302 may also be determined, if desired. The existence of such non-uniformities (e.g., regions of significantly higher or lower conductivity) can be due to poorly sintered diamond grains, high metal-solvent catalyst content regions, porosity, and/or cracks.

It will be readily apparent to one of skill in the art that actual calculation of the electrical conductivity of the PCD table 302 may not be necessary in every case, as one may alternatively compare the measured electrical resistance (or another characteristic that correlates to electrical conductivity)

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ity) to a threshold value known to correlate to the threshold electrical conductivity value for a given PCD microstructure. In another embodiment, the electrical conductivity may be measured directly.

FIG. 3B is a functional block diagram of an embodiment of a multi-probe resistance measurement electrical impedance testing ("EIT") system 400 that may be used to measure electrical resistance or impedance. The system 400 includes an EIT unit 401 configured to measure an electrical resistance of the PCD table 302 at a plurality of locations. The EIT unit 401 may include a plurality of probes 402 (e.g., 421 spring-loaded probes) configured to electrically contact a surface 303 of the PCD table 302 of the PDC 300 (shown in FIG. 4), and a plurality of probes 404 (e.g., two probes) to contact the substrate 304 of the PDC sample 300. For example, the probes 402 may be spring-loaded pins (e.g., "pogo" pins used in printed circuit board testing) that make contact with the surface 303 of the PCD table 302. Resistance measurements may be acquired and recorded at a plurality of different locations when 121 of the probes 402 and the probes 404 are used in the system 400. The electrical resistance measurements may then be reconstructed into a 3D electrical conductivity distribution of the PCD table 302 using a reconstruction algorithm.

The system 400 may be configured to make 4-probe DC resistance measurements in the approximate range from 0.1 mΩ to 1Ω on the PDC sample 300. The substrate 304 of the PDC sample 300 may be used as a reference conductor. One of the current probes and one of the voltage probes may be electrically connected to the substrate 304. The 4-probe measurement setup may be completed by multiplexing one of the top surface-contacting probes 402 for current injection and another of the top surface-contacting probes 402 for voltage measurement. Probe locations for the probes 402 are shown in the schematic diagram of FIG. 4 as + shapes and only one location is labeled as 402' for sake of clarity. Using this probe arrangement, only one large current multiplexer and one large voltage multiplexer may be required.

Referring again to FIG. 3B, the system 400 includes a data acquisition module 406 (e.g., a USB data acquisition) coupled to the EIT unit 401. The data acquisition module 406 includes an analog output 408 that controls the output current of a precision current source 410 in the range from about -150 mA to about +150 mA. The current is routed to one of the 121 sensor probes 402 in contact with the PCD table 302 through a 1:128 current multiplexer 412. For example, the current multiplexer 412 may be built using commercially available 8:1 analog multiplexers with 5Ω maximum series 'on' resistance. One of the reference probes 404 contacting the substrate 304 serves as a current sink and is grounded. A respective voltage measurement is taken between the sensor probe 402 selected by the 128:1 voltage multiplexer 424 and the second reference probe 404 contacting the substrate. The voltage is amplified by a programmable-gain instrumentation amplifier 414 and sent to an analog input 416 of the data acquisition module 406. The amplifier 414 may be programmed for gains of, for example, about 1, about 250, about 1000, and about 4000. Unity gain may be used for probe contact resistance measurement. A plurality of digital outputs 418 (e.g., 18 total) from the data acquisition module 406 control all the multiplexers and the amplifier gain of the amplifier 424.

A computer 420 (e.g., a desktop computer) is coupled to or includes the data acquisition module 406 therein. The computer 420 receives the electrical resistance measurements taken by the EIT unit 401 from the analog input 416 of the data acquisition module 406. The computer 420

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includes memory 421 storing software thereon containing computer executable instructions configured for reconstructing/calculating/analyzing the electrical conductivity distribution in the PCD table 302 of the PDC sample 300 being tested in accordance with a reconstruction algorithm and one or more processors 423 for executing the computer executable instructions. For example, the one or more processors 423 may control the data acquisition module 406 and process the measured resistance data to reconstruct and analyze the electrical conductivity distribution.

To calibrate the instrument, one or more precision reference resistors 422 are provided, such as 50 mΩ, 20 mΩ and 10 mΩ in an embodiment. A secondary 4:1 voltage multiplexer 425 may be provided to accommodate 4-wire measurements of these reference resistors 422. FIG. 3B shows only one exemplary reference resistor, but the connections of the other reference resistors may be similar.

Referring to FIG. 5, an embodiment for a sensor assembly 500 of the EIT unit 401 including a plurality of probes 402 is illustrated. In an embodiment, the probes 402 may be arranged in a triangular-grid pattern. It should be noted that other sensor-assembly configurations may be used, e.g., for PDC samples having a different size and/or a different configuration.

FIGS. 6A and 6B illustrate an embodiment of a sample holder 600 that facilitates placement of the PDC sample 300 to be tested using the system 400 so that reliable electrical contact with the sensor probes 402 and 404 may be established. The main body 602 has a cavity 604 therein configured for holding the PDC sample 300. The PDC sample 300 may be centered and held in place by a resilient member 606 (e.g., a soft O-ring) that is disposed in a groove formed in the main body 602 that encircles the PDC sample 300 and defines part of the cavity 604. The resilient member 606 allows turning the part holder upside-down to place the part on top of the spring-loaded probes 402. The probes 402 are installed in and project outwardly from a base 608 having corresponding holes (e.g., 121 holes) drilled therein. The sensor assembly 600 may include a cap 610 that carries the reference probes 404 that contact the substrate 304 of the PDC sample 300. One or more dowel pins 612 or other alignment structure may extend through sample holder components 602, 608, and 610 to keep them in alignment. Referring specifically to FIG. 6A, the components of the sample holder 600 may be compressed together so that the probes 402 and 404 are in electrical contact with the PDC sample 300 by, for example, thumb screws 614 or other compression mechanism.

Optionally, a conductive paste and/or coating (e.g., a conductive grease containing silver, copper, gold, or combinations thereof) may be applied to the surface 303 of the PCD table 302 to help reduce any occurrence of poor probe contact.

The described system 400 was used to test a variety of PDC samples. Each PDC sample included a cobalt-cemented carbide substrate having a PCD table bonded thereto. The PCD tables were comprised of a plurality of bonded-together diamond grains having cobalt infiltrated from the substrate and disposed interstitially between the bonded-together diamond grains. The electrical conductivity distributions of PCD tables from two PDCs having substantially homogenous PCD tables are shown in FIGS. 7A and 7B. Five slices through the 3D electrical conductivity distribution are shown at varying depths into the PCD table measured from an upper surface of the PCD table (e.g., the upper surface 303 in FIG. 3A). The depth is indicated above each slice. Even though the electrical conductivity is sub-

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stantially homogeneous, the average electrical conductivity varied from sample to sample, and was found to be strongly influenced by metal-solvent catalyst content.

Additional details of suitable EIT testing systems and additional results are disclosed in U.S. patent application Ser. No. 12/830,878 filed on 6 Jul. 2010 and titled METHODS FOR NON-DESTRUCTIVELY TESTING A POLYCRYSTALLINE DIAMOND ELEMENT, RELATED ELECTRICAL IMPEDANCE TOMOGRAPHY SYSTEMS, AND ROTARY DRILL BIT INCLUDING SELECTIVELY ORIENTED POLYCRYSTALLINE DIAMOND CUTTER, incorporated herein, in its entirety, by this reference. It should be noted that the described EIT testing system is only one suitable system for determining electrical conductivity. Other measurement systems and techniques may be employed.

#### Embodiments of Methods for Fabricating PCD

As previously discussed, and now discussed in more detail, the PCD may be formed by sintering a mass of a plurality of diamond particles in the presence of a metal-solvent catalyst. The diamond particles may exhibit an average particle size of about 50 μm or less, about 10 μm to about 20 μm, about 15 μm to about 19.5 μm, about 15 μm to about 18 μm, about 10 μm to about 18 μm, or about 5 μm to about 18 μm. In some embodiments, the average particle size of the diamond particles may be about 10 μm or less, such as about 2 μm to about 5 μm or submicron.

In an embodiment, the diamond particles of the mass of diamond particles may comprise a relatively larger size and at least one relatively smaller size. As used herein, the phrases "relatively larger" and "relatively smaller" refer to particle sizes (by any suitable method) that differ by at least a factor of two (e.g., 30 μm and 15 μm). According to various embodiments, the mass of diamond particles may include a portion exhibiting a relatively larger size (e.g., 30 μm, 20 μm, 15 μm, 12 μm, 10 μm, 8 μm) and another portion exhibiting at least one relatively smaller size (e.g., 6 μm, 5 μm, 4 μm, 3 μm, 2 μm, 1 μm, 0.5 μm, less than 0.5 μm, 0.1 μm, less than 0.1 μm). In one embodiment, the mass of diamond particles may include a portion exhibiting a relatively larger size between about 10 μm and about 40 μm and another portion exhibiting a relatively smaller size between about 1 μm and 4 μm. In some embodiments, the mass of diamond particles may comprise three or more different sizes (e.g., one relatively larger size and two or more relatively smaller sizes), without limitation.

It is noted that the as-sintered diamond grain size may differ from the average particle size of the mass of diamond particles prior to sintering due to a variety of different physical processes, such as grain growth, diamond particles fracturing, carbon provided from another carbon source (e.g., dissolved carbon in the metal-solvent catalyst), or combinations of the foregoing. The metal-solvent catalyst (e.g., iron, nickel, cobalt, or alloys thereof) may be provided in particulate form mixed with the diamond particles, as a thin foil or plate placed adjacent to the mass of diamond particles, from a cemented carbide substrate including a metal-solvent catalyst, or combinations of the foregoing.

In order to efficiently sinter the mass of diamond particles, the mass may be enclosed in a pressure transmitting medium, such as a refractory metal can, graphite structure, pyrophyllite, and/or other suitable pressure transmitting structure to form a cell assembly. Examples of suitable gasket materials and cell structures for use in manufacturing PCD are disclosed in U.S. Pat. No. 6,338,754 and U.S.



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patent application Ser. No. 11/545,929, each of which is incorporated herein, in its entirety, by this reference. Another example of a suitable pressure transmitting material is pyrophyllite, which is commercially available from Wonderstone Ltd. of South Africa. In an embodiment, the pressure transmitting material/gasket material may comprise pyrophyllite generally in the shape of a cube having a cavity for receiving the contents to be HPHT processed, with an edge length of the cube being about 1.5 inch to about 2.0 inch, about 1.5 inch to about 1.8 inch, about 1.6 inch to about 1.8 inch, or about 1.75 inch to about 1.8 inch (e.g., about 1.775 inch). The cell assembly, including the pressure transmitting medium and mass of diamond particles therein, is subjected to an HPHT process using an ultra-high pressure press at a temperature of at least about 1000° C. (e.g., about 1100° C. to about 2200° C., or about 1200° C. to about 1450° C.) and a pressure in the pressure transmitting medium of at least about 7.5 GPa (e.g., about 7.5 GPa to about 15 GPa) for a time sufficient to sinter the diamond particles together in the presence of the metal-solvent catalyst and form the PCD comprising bonded diamond grains defining interstitial regions occupied by the metal-solvent catalyst. For example, the pressure in the pressure transmitting medium employed in the HPHT process may be at least about 8.0 GPa, at least about 9.0 GPa, at least about 10.0 GPa, at least about 11.0 GPa, at least about 12.0 GPa, or at least about 14 GPa.

The pressure values employed in the HPHT processes disclosed herein refer to the pressure in the pressure transmitting medium at room temperature (e.g., about 25° C.) with application of pressure using an ultra-high pressure press and not the pressure applied to exterior of the cell assembly. The actual pressure in the pressure transmitting medium at sintering temperature may be slightly higher. The ultra-high pressure press may be calibrated at room temperature by embedding at least one calibration material that changes structure at a known pressure, such as PbTe, thallium, barium, or bismuth in the pressure transmitting medium. Further, optionally, a change in resistance may be measured across the at least one calibration material due to a phase change thereof. For example, PbTe exhibits a phase change at room temperature at about 6.0 GPa and bismuth exhibits a phase change at room temperature at about 7.7 GPa. Examples of suitable pressure calibration techniques are disclosed in G. Rousse, S. Klotz, A. M. Saitta, J. Rodriguez-Carvajal, M. I. McMahon, B. Couzinet, and M. Mezouar, "Structure of the Intermediate Phase of PbTe at High Pressure," *Physical Review B: Condensed Matter and Materials Physics*, 71, 224116 (2005) and D. L. Decker, W. A. Bassett, L. Merrill, H. T. Hall, and J. D. Barnett, "High-Pressure Calibration: A Critical Review," *J. Phys. Chem. Ref. Data*, 1, 3 (1972).

In an embodiment, a pressure of at least about 7.5 GPa in the pressure transmitting medium may be generated by applying pressure to a cubic high-pressure cell assembly that encloses the mass of diamond particles to be sintered using anvils, with each anvil applying pressure to a different face of the cubic high-pressure assembly. In such an embodiment, a surface area of each anvil face of the anvils may be selectively dimensioned to facilitate application of pressure of at least about 7.5 GPa to the mass of diamond particles being sintered. For example, the surface area of each anvil may be less than about 12.0 cm<sup>2</sup> (e.g., about 8 cm<sup>2</sup> to about 10 cm<sup>2</sup>), or greater than 12.0 cm<sup>2</sup> such as about 14.7 cm<sup>2</sup> to about 17 cm<sup>2</sup>. In an embodiment, a suitable ratio of an edge length of a face of the uncompressed cubic cell assembly containing the contents prior to being HPHT processed to an

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edge length of the anvil face may be about 1.20 to about 1.50, such as about 1.3 to about 1.4 (e.g., about 1.31, about 1.32, about 1.33, about 1.34, about 1.35, about 1.36, about 1.37, about 1.38, about 1.39, about 1.31 to about 1.34), greater than about 1.2, greater than about 1.3, or about 1.4 to about 1.5. The anvils may be made from a cobalt-cemented tungsten carbide or other material having a sufficient compressive strength to help reduce damage thereto through repetitive use in a high-volume commercial manufacturing environment. Optionally, as an alternative to or in addition to selectively dimensioning the surface area of each anvil face, two or more internal anvils may be embedded in the cubic high-pressure cell assembly to further intensify pressure. For example, the article W. Utsumi, N. Toyama, S. Endo and F. E. Fujita, "X-ray diffraction under ultrahigh pressure generated with sintered diamond anvils," *J. Appl. Phys.*, 60, 2201 (1986) is incorporated herein, in its entirety, by this reference and discloses that sintered diamond anvils may be embedded in a cubic pressure transmitting medium for intensifying the pressure applied by an ultra-high pressure press to a workpiece also embedded in the cubic pressure transmitting medium.

#### PDC Embodiments and Methods of Fabricating PDCs

Referring to FIG. 8A, the PCD embodiments may be employed in a PDC for cutting applications, bearing applications, or many other applications. FIG. 8A is a cross-sectional view of the PDC 300 shown in FIG. 3A. The PCD table 302 may be formed of PCD in accordance with any of the PCD embodiments disclosed herein. The PCD table 302 exhibits at least one lateral dimension "d" (e.g., a diameter), and may include an optional chamfer 307 formed between a working surface 303 and a lateral surface 305.

Although FIG. 8A shows the working surface 303 as substantially planar, the working surface 303 may be concave, convex, or another nonplanar geometry. The substrate 304 may be generally cylindrical or another selected configuration, without limitation. Although FIGS. 8A, and 8C show an interfacial surface 308 of the substrate 304 as being substantially planar, the interfacial surface 308 may exhibit a selected nonplanar topography, such as a grooved, ridged, or other nonplanar interfacial surface. The substrate 304 may include, without limitation, cemented carbides, such as tungsten carbide, titanium carbide, chromium carbide, niobium carbide, tantalum carbide, vanadium carbide, or combinations thereof cemented with iron, nickel, cobalt, or alloys thereof. For example, in one embodiment, the substrate 304 comprises cobalt-cemented tungsten carbide.

As illustrated in FIG. 8B, the PCD table 302 shown in FIG. 8A may be acid leached to a selected depth "d" measured from the upper surface 323 and/or the chamfer 327 to form a leached region 325 that is depleted of the metal-solvent catalyst to form a PDC 320. For example, the leached region 325 may generally contour the upper surface 323, the chamfer 327, and the at least one lateral surface 305. The leached region 325 may extend along a selected length of the at least one lateral surface 305. A residual amount of the metal-solvent catalyst may be present in the leached region 325 even after leaching. For example, the metal-solvent catalyst may comprise about 0.8 weight % to about 1.50 weight % and, more particularly, about 0.9 weight % to about 1.2 weight % of the PCD table.

The leaching may be performed in a suitable acid (e.g., aqua regia, nitric acid, hydrofluoric acid, or combinations thereof) so that the leached region 325 of the PCD table 302,



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as shown in FIG. 8B is substantially free of the metal-solvent catalyst. As a result of the metal-solvent catalyst being depleted from the at least partially leached PCD region 325, the PCD table 302 is relatively more thermally stable.

FIG. 8C is an enlarged cross-sectional view of the PCD 300 shown in FIG. 8A. FIG. 8C illustrates the thickness "t" of the PCD table 302 that extends from the working surface 303 to the interfacial surface 308. In an embodiment, the electrical conductivity of the PCD table 302 decreases gradually with distance from the working surface 303 (a region of relatively higher electrical conductivity) to the interfacial surface 308 (a region of relatively lower electrical conductivity), thereby creating an electrical conductivity gradient profile as shown in FIG. 8D.

As illustrated in FIG. 8D, the magnitude of the electrical conductivity is represented by the length of arrows 301, with the greatest magnitude of electrical conductivity at the working surface 303 and the smallest magnitude of electrical conductivity at the interfacial surface 308. This electrical conductivity gradient profile may exist independently of the thickness "t" of the PCD table 302, such as for both thin and thick PCD bodies.

Generally, as the sintering cell pressure that is used to form the PCD increases, the amount of metal-solvent catalyst in the PCD may decrease. For a given PCD microstructure, the amount of metal-solvent catalyst present in the PCD may be correlated with the measured electrical conductivity ( $\sigma$ ) of the PCD. Accordingly, a relatively small amount of metal-solvent catalyst within the PCD generally indicates a relatively small value of electrical conductivity.

Electrostatic conductivity measurements may depend on having adequate contact between pin probes (FIG. 5) and residual metal-solvent catalyst in the PCD table. As metal-solvent catalyst content is reduced, it is possible that pin probes may contact more diamond and less metal-solvent catalyst. As the graph in FIG. 9 illustrates, as sintering cell pressure increases from approximately 1 GPa to approximately 8 GPa, and metal-solvent catalyst content decreases, the electrical conductivity of the PCD may also decrease in a relatively non-linear fashion. These values of cell pressure are shown to approach a value of about 8 GPa as values for electrical conductivity reach a substantially constant value with increasing cell pressure. The inventors believe that the decrease in metal-solvent catalyst content under high pressure may be the reason for the non-linearity of conductivity observed at higher cell pressures (e.g., lower cobalt concentrations) as seen in FIG. 9.

As shown in FIG. 10, values for cell pressure and wear volume (the amount of material removed from the PCD table in a VTL test) may be similarly correlated. FIG. 10 illustrates that as cell pressure increases from approximately 1 GPa to approximately 8 GPa, the wear volume is also found to decrease in a relatively non-linear fashion. As values of cell pressure approach a value of approximately 8 GPa, the values for wear volume reach a substantially constant value with increasing cell pressure. The data shown in FIG. 10 may be measured after cutting a fixed volume of rock. As the cell pressure increases, the wear resistance may continue to increase until essentially no wear exists after cutting this fixed volume of rock.

FIG. 11A is a schematic illustration of an embodiment of a method for fabricating the PDC 300 shown in FIGS. 3A and 8A. Referring to FIG. 11, a mass of diamond particles 1100 having any of the above-mentioned average particle sizes and distributions (e.g., an average particle size of about 50  $\mu\text{m}$  or less) is positioned adjacent to the interfacial

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surface 308 of the substrate 304. As previously discussed, the substrate 304 may include a metal-solvent catalyst. The mass of diamond particles 1100 and substrate 304 may be subjected to an HPHT process using conditions previously described with respect to sintering the PCD embodiments disclosed herein. The PDC 300 so-formed includes the PCD table 302 that comprises PCD, formed of any of the PCD embodiments disclosed herein, integrally formed with the substrate 304 and bonded to the interfacial surface 308 of the substrate 304. If the substrate 304 includes a metal-solvent catalyst, the metal-solvent catalyst may liquefy and infiltrate the mass of diamond particles 1100 to promote growth between adjacent diamond particles of the mass of diamond particles 1100 to form the PCD table 302 comprised of a body of bonded diamond grains having the infiltrated metal-solvent catalyst interstitially disposed between bonded diamond grains. For example, if the substrate 304 is a cobalt-cemented tungsten carbide substrate, cobalt from the substrate 304 may be liquefied and infiltrate the mass of diamond particles 1100 to catalyze formation of the PCD table 302.

Employing selectively dimensioned anvil faces and/or internal anvils in the ultra-high pressure press used to process the mass of diamond particles 1100 and substrate 304 enables forming the at least one lateral dimension "d" of the PCD table 302 to be about 0.80 cm or more. Referring again to FIG. 8A, for example, the at least one lateral dimension "d" may be about 0.80 cm to about 3.0 cm and, in some embodiments, about 1.3 cm to about 1.9 cm or about 1.6 cm to about 1.9 cm. A representative volume of the PCD table 302 (or any PCD article of manufacture disclosed herein) formed using the selectively dimensioned anvil faces and/or internal anvils may be at least about 0.050  $\text{cm}^3$ . For example, the volume may be about 0.25  $\text{cm}^3$  to at least about 1.25  $\text{cm}^3$  or about 0.1  $\text{cm}^3$  to at least about 0.70  $\text{cm}^3$ . A representative volume for the PDC 300 may be about 0.4  $\text{cm}^3$  to at least about 4.6  $\text{cm}^3$ , such as about 1.1  $\text{cm}^3$  to at least about 2.3  $\text{cm}^3$ .

In other embodiments, a PCD table according to an embodiment may be separately formed using an HPHT sintering process and, subsequently, bonded to the interfacial surface 308 of the substrate 304 by brazing, using a separate HPHT bonding process, or any other suitable joining technique, without limitation. In yet another embodiment, a substrate may be formed by depositing a binderless carbide (e.g., tungsten carbide) via chemical vapor deposition onto the separately formed PCD table.

FIG. 11B is a schematic illustration of another embodiment of a method for fabricating a PDC 1140. FIG. 11B illustrates a layered PCD precursor assembly 1120 of a first layer 1122 of a mass of diamond particles having a fine average particle size (e.g., an average particle size of about 10  $\mu\text{m}$  to about 20  $\mu\text{m}$ , less than about 30  $\mu\text{m}$ , about 20 to about 40  $\mu\text{m}$ , or about 11  $\mu\text{m}$  to about 19.5  $\mu\text{m}$ , greater than 10  $\mu\text{m}$ , about 10  $\mu\text{m}$  to about 20  $\mu\text{m}$ , less than about 20  $\mu\text{m}$ , less than about 25  $\mu\text{m}$ , about 15  $\mu\text{m}$  to about 25  $\mu\text{m}$ , or about 20  $\mu\text{m}$ ) adjacent to a second layer 1124 of a mass of diamond particles having a coarse average particle size that is greater than the fine average particle size of the first layer 1122 (e.g., at least about 40  $\mu\text{m}$ , about 40  $\mu\text{m}$  to about 60  $\mu\text{m}$ , about 30  $\mu\text{m}$  to about 50  $\mu\text{m}$ , greater than about 20  $\mu\text{m}$ , greater than about 30  $\mu\text{m}$ , about 20  $\mu\text{m}$  to about 40  $\mu\text{m}$ , about 20  $\mu\text{m}$  to about 50  $\mu\text{m}$ , about 35  $\mu\text{m}$  to about 45  $\mu\text{m}$ , about 40  $\mu\text{m}$ , about 1.5 to about 4 times the fine average particle size, about 2 to about 2.5 times the fine average particle size, etc.). The second layer 1124 may include about 2% to about 8% by weight tungsten, tungsten carbide, sintered tungsten

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carbide, or combinations thereof. Although the illustrated embodiment of the PCD precursor assembly 1120 only utilizes two layers of diamond particles, two or more, or more than three layers may be employed. In one embodiment, each layer may have a progressively smaller average diamond particle size with distance away from the substrate 1104.

As shown in FIG. 11B, the layered PCD precursor assembly 1120 is positioned adjacent to the interfacial surface 1108 of the substrate 1104. As previously discussed, the substrate 1104 may include a metal-solvent catalyst. The layered PCD precursor assembly 1120 and the substrate 1104 may be subjected to an HPHT process using conditions previously described with respect to sintering the PCD embodiments disclosed herein. The PDC 1140 so-formed includes the PCD table 1130 that comprises PCD that is integrally formed with the substrate 1104 and bonded to the interfacial surface 1108 of the substrate 1104. If the substrate 1104 includes a metal-solvent catalyst, the metal-solvent catalyst may liquefy and infiltrate the layered PCD precursor assembly 1120 to promote growth between adjacent diamond particles of the layered PCD precursor assembly 1120 to form the PCD table 1130 comprised of a body of bonded diamond grains having the infiltrated metal-solvent catalyst interstitially disposed between the bonded diamond grains. For example, if the substrate 1104 is a cobalt-cemented tungsten carbide substrate, cobalt from the substrate 1104 may be liquefied and infiltrate the layered PCD precursor assembly 1120 to catalyze formation of the PCD table 1140. Providing a coarser layer of diamond particles (e.g., coarse diamond particle of the second layer 1124) adjacent to the substrate 1104 may prevent or at least reduce braze cracking when the PDC 1140 is brazed to a structure such as bit body of a rotary drill bit.

The PCD precursor assembly 1120 may be subjected to HPHT processing at any of the HPHT conditions disclosed herein. The PCD table 1130 of the PDC 1140 so-formed may exhibit two distinct diamond grain layers, a first layer 1132 adjacent to the substrate including coarse-sized diamond grains exhibiting a coarse-sized average grain size, and a second layer 1134 adjacent to the first layer including fine-sized diamond grains exhibiting a fine-sized average grain size smaller than the coarse-sized average grain size. The average diamond grain sizes may be the same or similar to that of average diamond particle sizes used to form it. For example, an average diamond grain size of the first layer 1132 may be the same or similar to that of the coarse diamond particle size of the second layer 1124 and the average diamond grain size of the second layer 1134 may be the same or similar to that of the fine average diamond particle size of the first layer 1122. As another example, the average diamond grain size of the first layer 1132 may have a coarse average diamond grain size of greater than about 20  $\mu\text{m}$ , greater than about 30  $\mu\text{m}$ , about 20  $\mu\text{m}$  to about 40  $\mu\text{m}$ , about 30  $\mu\text{m}$  to about 40  $\mu\text{m}$ , about 20  $\mu\text{m}$  to about 50  $\mu\text{m}$ , about 40  $\mu\text{m}$  to about 50  $\mu\text{m}$ , or about 35  $\mu\text{m}$  to about 45  $\mu\text{m}$ . The average diamond grain size of the second layer 1134 may have a fine average diamond grain size of greater than about 10  $\mu\text{m}$ , about 10  $\mu\text{m}$  to about 20  $\mu\text{m}$ , less than about 20  $\mu\text{m}$ , less than about 25  $\mu\text{m}$ , about 15  $\mu\text{m}$  to about 25  $\mu\text{m}$ , and about 15  $\mu\text{m}$  to about 20  $\mu\text{m}$ .

In another embodiment, a PCD table may be fabricated according to any of the disclosed embodiments in a first HPHT process, leached to remove substantially all of the metal-solvent catalyst from the interstitial regions between the bonded diamond grains, and subsequently bonded to a substrate in a second HPHT process. In the second HPHT

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process, an infiltrant from, for example, a cemented carbide substrate may infiltrate into the interstitial regions from which the metal-solvent catalyst was depleted. For example, the infiltrant may be cobalt that is swept-in from a cobalt-cemented tungsten carbide substrate. In one embodiment, the first and/or second HPHT process may be performed at a pressure of at least about 7.5 GPa. In one embodiment, the infiltrant may be leached from the infiltrated PCD table using a second acid leaching process following the second HPHT process.

In some embodiments, the pressure employed in the HPHT process used to fabricate the PDC 300 may be sufficient to reduce residual stresses in the PCD table 302 that develop during the HPHT process due to the thermal expansion mismatch between the substrate 304 and the PCD table 302. In such an embodiment, the principal stress measured on the working surface 303 of the PDC 300 may exhibit a value of about -345 MPa to about 0 MPa, such as about -289 MPa. For example, the principal stress measured on the working surface 303 may exhibit a value of about -345 MPa to about 0 MPa. A conventional PDC fabricated using an HPHT process at a pressure below about 7.5 GPa may result in a PCD table thereof exhibiting a principal stress on a working surface thereof of about -1724 MPa to about -414 MPa, such as about -770 MPa.

Residual stress may be measured on the working surface 303 of the PCD table 302 of the PDC 300 as described in T. P. Lin, M. Hood, G. A. Cooper, and R. H. Smith, "Residual stresses in polycrystalline diamond compacts," J. Am. Ceram. Soc. 77, 6, 1562-1568 (1994). More particularly, residual strain may be measured with a rosette strain gage bonded to the working surface 303. Such strain may be measured for different levels of removal of the substrate 304 (e.g., as material is removed from the back of the substrate 304). Residual stress may be calculated from the measured residual strain data.

FIG. 12 is a graph of residual principal stress versus substrate thickness that was measured in a PCD table of a PDC fabricated at pressure above about 7.5 GPa in accordance with an embodiment of the invention and a PCD table of a conventionally formed PDC. The residual principal stress was determined using the technique described in the article referenced above by Lin et al. Curve 1210 shows the measured residual principal stress on a working surface of the PDC fabricated at a pressure above about 7.5 GPa. The PDC that was fabricated at a pressure above about 7.5 GPa had a thickness dimension of about 1 mm and the substrate had a thickness dimension of about 7 mm and a diameter of about 13 mm. Curve 1212 shows the measured residual principal stress on a working surface of a PCD table of a conventionally PDC fabricated at pressure below about 7.5 GPa. The PDC that was fabricated at a pressure below about 7.5 GPa had a thickness dimension of about 1 mm and the substrate had a thickness dimension of about 7 mm and a diameter of about 13 mm. The highest absolute value of the residual principal stress occurs with the full substrate length of about 7 mm. As shown by the curves 1210 and 1212, increasing the pressure, employed in the HPHT process used to fabricate a PDC, above about 7.5 GPa may reduce the highest absolute value of the principal residual stress in a PCD table thereof by about 60% relative to a conventionally fabricated PDC. For example, at the full substrate length, the absolute value of the principal residual stress in the PCD table fabricated at a pressure above about 7.5 GPa is about 60% less than the absolute value of the principal residual stress in the PCD table of the conventionally fabricated PDC.

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The following working examples provide further detail about the magnetic properties of PCD tables of PDCs fabricated in accordance with the principles of some of the specific embodiments of the invention. The magnetic properties of each PCD table listed in Tables I-IV were tested using a KOERZIMAT CS 1.096 instrument that is commercially available from Foerster Instruments of Pittsburgh, Pa. The specific magnetic saturation of each PCD table was measured in accordance with ASTM B886-03 (2008) and the coercivity of each PCD table was measured using ASTM B887-03 (2008) using a KOERZIMAT CS 1.096 instrument. The amount of cobalt-based metal-solvent catalyst in the tested PCD tables was determined using energy dispersive spectroscopy and Rutherford backscattering spectroscopy.

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form a PCD table bonded to the substrate. The surface area of each anvil of the HPHT press and the hydraulic line pressure used to drive the anvils were selected so that the sintering pressure was at least about 7.8 GPa. The temperature of the HPHT process was about 1400° C. and the sintering pressure was at least about 7.8 GPa. The sintering pressures listed in Table I refer to the pressure in the high-pressure cell medium at room temperature, and the actual sintering pressures at the sintering temperature are believed to be greater. After the HPHT process, the PCD table was removed from the substrate by grinding away the substrate. However, the substrate may also be removed using electro-discharge machining or another suitable method.

TABLE I

Selected Magnetic Properties of PCD Tables Fabricated According to Embodiments of the Invention						
	Average Diamond Particle Size (μm)	Sintering Pressure (GPa)	Specific Magnetic Saturation (G · cm <sup>3</sup> /g)	Calculated Co wt %	Coercivity (Oe)	Specific Permeability (G · cm <sup>3</sup> /g · Oe)
1	20	7.8	11.15	5.549	130.2	0.08564
2	19	7.8	11.64	5.792	170.0	0.06847
3	19	7.8	11.85	5.899	157.9	0.07505
4	19	7.8	11.15	5.550	170.9	0.06524
5	19	7.8	11.43	5.689	163.6	0.06987
6	19	7.8	10.67	5.150	146.9	0.07263
7	19	7.8	10.76	5.357	152.3	0.07065
8	19	7.8	10.22	5.087	145.2	0.07039
9	19	7.8	10.12	5.041	156.6	0.06462
10	19	7.8	10.72	5.549	137.1	0.07819
11	11	7.8	12.52	6.229	135.3	0.09254
12	11	7.8	12.78	6.362	130.5	0.09793
13	11	7.8	12.69	6.315	134.6	0.09428
14	11	7.8	13.20	6.569	131.6	0.1003

copy. The specific magnetic saturation constant of the cobalt-based metal-solvent catalyst in the tested PCD tables was determined to be about 201 G·cm<sup>3</sup>/g using an iterative analysis as previously described. When a value of 201 G·cm<sup>3</sup>/g was used for the specific magnetic saturation constant of the cobalt-based metal-solvent catalyst, the calculated amount of the cobalt-based metal-solvent catalyst in the tested PCD tables using the analysis software of the KOERZIMAT CS 1.096 instrument substantially matched the measurements using energy dispersive spectroscopy and Rutherford spectroscopy.

Table I below lists PCD tables that were fabricated in accordance with the principles of certain embodiments of the invention discussed above. Each PCD table was fabricated by placing a mass of diamond particles having the listed average diamond particle size adjacent to a cobalt-cemented tungsten carbide substrate in a niobium container, placing the container in a high-pressure cell medium, and subjecting the high-pressure cell medium and the container therein to an HPHT process using an HPHT cubic press to

form a PCD table bonded to the substrate. The surface area of each anvil of the HPHT press and the hydraulic line pressure used to drive the anvils were selected so that the sintering pressure was about 4.6 GPa. Except for samples 15, 16, 18, and 19, which were subjected to a temperature of about 1430° C., the temperature of the HPHT process was about 1400° C. and the sintering pressure was about 4.6 GPa. The sintering pressures listed in Table II refer to the pressure in the high-pressure cell medium at room temperature. After the HPHT process, the PCD table was removed from the cobalt-cemented tungsten carbide substrate by grinding away the cobalt-cemented tungsten carbide substrate.

TABLE II

Selected Magnetic Properties of Several Conventional PCD Tables						
	Average Diamond Particle Size (μm)	Sintering Pressure (GPa)	Specific Magnetic Saturation (G · cm <sup>3</sup> /g)	Calculated Co wt %	Coercivity (Oe)	Specific Permeability (G · cm <sup>3</sup> /g · Oe)
15	20	4.61	19.30	9.605	94.64	0.2039
16	20	4.61	19.52	9.712	96.75	0.2018



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TABLE II-continued

Selected Magnetic Properties of Several Conventional PCD Tables						
Average Diamond Particle Size ( $\mu\text{m}$ )	Sintering Pressure (GPa)	Specific Magnetic Saturation ( $\text{G} \cdot \text{cm}^3/\text{g}$ )	Calculated Co wt %	Coercivity (Oe)	Specific Permeability ( $\text{G} \cdot \text{cm}^3/\text{g} \cdot \text{Oe}$ )	
17	20	4.61	19.87	9.889	94.60	0.2100
18	20	5.08	18.61	9.260	94.94	0.1960
19	20	5.08	18.21	9.061	100.4	0.1814
20	20	5.86	16.97	8.452	108.3	0.1567
21	20	4.61	17.17	8.543	102.0	0.1683
22	20	4.61	17.57	8.745	104.9	0.1675
23	20	5.08	16.10	8.014	111.2	0.1448
24	20	5.08	16.79	8.357	107.1	0.1568

As shown in Tables I and II, the conventional PCD tables listed in Table II exhibit a higher cobalt content therein than the PCD tables listed in Table I as indicated by the relatively higher specific magnetic saturation values. Additionally, the conventional PCD tables listed in Table II exhibit a lower coercivity indicative of a relatively greater mean free path between diamond grains, and thus may indicate relatively less diamond-to-diamond bonding between the diamond grains. Thus, the PCD tables according to examples of the invention listed in Table I may exhibit significantly less cobalt therein and a lower mean free path between diamond grains than the PCD tables listed in Table II.

Table III below lists conventional PCD tables that were obtained from PDCs. Each PCD table listed in Table III was separated from a cobalt-cemented tungsten carbide substrate bonded thereto by grinding.

TABLE III

Selected Magnetic Properties of Several Conventional PCD Tables				
Specific Magnetic Saturation ( $\text{G} \cdot \text{cm}^3/\text{g}$ )	Calculated Co wt %	Coercivity (Oe)	Specific Permeability ( $\text{G} \cdot \text{cm}^3/\text{g} \cdot \text{Oe}$ )	
25	17.23	8.572	140.4	0.1227
26	16.06	7.991	150.2	0.1069
27	15.19	7.560	146.1	0.1040
28	17.30	8.610	143.2	0.1208
29	17.13	8.523	152.1	0.1126
30	17.00	8.458	142.5	0.1193
31	17.08	8.498	147.2	0.1160
32	16.10	8.011	144.1	0.1117

Table IV below lists conventional PCD tables that were obtained from PDCs. Each PCD table listed in Table IV was separated from a cobalt-cemented tungsten carbide substrate bonded thereto by grinding the substrate away. Each PCD table listed in Table IV and tested had a leached region from which cobalt was depleted and an unleached region in which cobalt is interstitially disposed between bonded diamond grains. The leached region was not removed. However, to determine the specific magnetic saturation and the coercivity of the unleached region of the PCD table having metal-solvent catalyst occupying interstitial regions therein, the leached region may be ground away so that only the unleached region of the PCD table remains. It is expected that the leached region causes the specific magnetic saturation to be lower and the coercivity to be higher than if the leached region was removed and the unleached region was tested.

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TABLE IV

Selected Magnetic Properties of Several Conventional Leached PCD Tables				
Specific Magnetic Saturation ( $\text{G} \cdot \text{cm}^3/\text{g}$ )	Calculated Co wt %	Coercivity (Oe)	Specific Permeability ( $\text{G} \cdot \text{cm}^3/\text{g} \cdot \text{Oe}$ )	
33	17.12	8.471	143.8	0.1191
34	13.62	6.777	137.3	0.09920
35	15.87	7.897	140.1	0.1133
36	12.95	6.443	145.5	0.0890
37	13.89	6.914	142.0	0.09782
38	13.96	6.946	146.9	0.09503
39	13.67	6.863	133.8	0.1022
40	12.80	6.369	146.3	0.08749

As shown in Tables I, III, and IV, the conventional PCD tables of Tables III and IV exhibit a higher cobalt content therein than the PCD tables listed in Table I as indicated by the relatively higher specific magnetic saturation values. This is believed by the inventors to be a result of the PCD tables listed in Tables III and IV being formed by sintering diamond particles having a relatively greater percentage of fine diamond particles than the diamond particle formulations used to fabricate the PCD tables listed in Table I.

A similar correlation between higher cobalt content and increased electrical conductivity properties of PCD tables has also been observed. Sensitivity of electrical conductivity measurements of PDC diamond tables of a given PCD microstructure may provide an excellent method for estimation and imaging of metal content in the diamond table. Such types of estimates are sensitive to changes in bulk average metal-solvent content and local changes in the metal-solvent content, allowing for a sensitive estimation of both metal content and cutting performance.

Referring back to FIGS. 9 and 10, electrical conductivity trends with metal-solvent content suggest that lowering the metal-solvent content, and thus the electrical conductivity, increases performance of a PDC. In fact, relatively lowered metal-solvent content in the PDC appears to substantially influence cutting performance. Therefore, it follows that the electrical conductivity, also dependent on metal-solvent catalyst content, may also be used as a quality characteristic for evaluating PDC cutting performance. For example, a PCD cutting element with electrical conductivities below about 1200 S/m (in an unleached region of PCD) have been found to increase cutting performance.

Embodiments of Applications for PCD and PDCs

The disclosed PCD and PDC embodiments may be used in a number of different applications including, but not

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limited to, use in a rotary drill bit (FIGS. 13 and 14), a thrust-bearing apparatus (FIG. 15), a radial bearing apparatus (FIG. 16), a subterranean drilling system (FIG. 17), and a wire-drawing die (FIG. 18). The various applications discussed above are merely some examples of applications in which the PCD and PDC embodiments may be used. Other applications are contemplated, such as employing the disclosed PCD and PDC embodiments in friction stir welding tools.

FIG. 13 is an isometric view and FIG. 14 is a top elevation view of an embodiment of a rotary drill bit 800. The rotary drill bit 800 includes at least one PDC configured according to any of the previously described PDC embodiments. The rotary drill bit 800 comprises a bit body 802 that includes radially and longitudinally extending blades 804 with leading faces 806, and a threaded pin connection 808 for connecting the bit body 802 to a drilling string. The bit body 802 defines a leading end structure for drilling into a subterranean formation by rotation about a longitudinal axis 810 and application of weight-on-bit. At least one PDC cutting element, configured according to any of the previously described PDC embodiments (e.g., the PDC 300 shown in FIG. 3A), may be affixed to the bit body 802. With reference to FIG. 14, a plurality of PDCs 812 are secured to the blades 804. For example, each PDC 812 may include a PCD table 814 bonded to a substrate 816. More generally, the PDCs 812 may comprise any PDC disclosed herein, without limitation. In addition, if desired, in some embodiments, a number of the PDCs 812 may be conventional in construction. Also, circumferentially adjacent blades 804 define so-called junk slots 818 therebetween, as known in the art. Additionally, the rotary drill bit 800 may include a plurality of nozzle cavities 820 for communicating drilling fluid from the interior of the rotary drill bit 800 to the PDCs 812.

FIGS. 13 and 14 merely depict an embodiment of a rotary drill bit that employs at least one cutting element comprising a PDC fabricated and structured in accordance with the disclosed embodiments, without limitation. The rotary drill bit 800 is used to represent any number of earth-boring tools or drilling tools, including, for example, core bits, roller-cone bits, fixed-cutter bits, eccentric bits, bicenter bits, reamers, reamer wings, or any other downhole tool including PDCs, without limitation.

The PCD and/or PDCs disclosed herein (e.g., the PDC 300 shown in FIG. 3A) may also be utilized in applications other than rotary drill bits. For example, the disclosed PDC embodiments may be used in thrust-bearing assemblies, radial bearing assemblies, wire-drawing dies, artificial joints, machining elements, and heat sinks.

FIG. 15 is an isometric cut-away view of an embodiment of a thrust-bearing apparatus 900, which may utilize any of the disclosed PDC embodiments as bearing elements. The thrust-bearing apparatus 900 includes respective thrust-bearing assemblies 902. Each thrust-bearing assembly 902 includes an annular support ring 904 that may be fabricated from a material, such as carbon steel, stainless steel, or another suitable material. Each support ring 904 includes a plurality of recesses (not labeled) that receive a corresponding bearing element 906. Each bearing element 906 may be mounted to a corresponding support ring 904 within a corresponding recess by brazing, press-fitting, using fasteners, or another suitable mounting technique. One or more, or all of bearing elements 906 may be configured according to any of the disclosed PDC embodiments. For example, each

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bearing element 906 may include a substrate 908 and a PCD table 910, with the PCD table 910 including a bearing surface 912.

In use, the bearing surfaces 912 of one of the thrust-bearing assemblies 902 bear against the opposing bearing surfaces 912 of the other one of the bearing assemblies 902. For example, one of the thrust-bearing assemblies 902 may be operably coupled to a shaft to rotate therewith and may be termed a "rotor." The other one of the thrust-bearing assemblies 902 may be held stationary and may be termed a "stator."

FIG. 16 is an isometric cut-away view of an embodiment of a radial bearing apparatus 1000, which may utilize any of the disclosed PDC embodiments as bearing elements. The radial bearing apparatus 1000 includes an inner race 1002 positioned generally within an outer race 1004. The outer race 1004 includes a plurality of bearing elements 1006 affixed thereto that have respective bearing surfaces 1008. The inner race 1002 also includes a plurality of bearing elements 1010 affixed thereto that have respective bearing surfaces 1012. One or more, or all of the bearing elements 1006 and 1010 may be configured according to any of the PDC embodiments disclosed herein. The inner race 1002 is positioned generally within the outer race 1004, and thus the inner race 1002 and outer race 1004 may be configured so that the bearing surfaces 1008 and 1012 may at least partially contact one another and move relative to each other as the inner race 1002 and outer race 1004 rotate relative to each other during use.

The radial bearing apparatus 1000 may be employed in a variety of mechanical applications. For example, so-called "roller-cone" rotary drill bits may benefit from a radial-bearing apparatus disclosed herein. More specifically, the inner race 1002 may be mounted to a spindle of a roller cone and the outer race 1004 may be mounted to an inner bore formed within a cone and such an outer race 1004 and inner race 1002 may be assembled to form a radial bearing apparatus.

Referring to FIG. 17, the thrust-bearing apparatus 900 and/or radial bearing apparatus 1000 may be incorporated in a subterranean drilling system. FIG. 17 is a schematic isometric cut-away view of a subterranean drilling system 1100 that includes at least one of the thrust-bearing apparatuses 900 shown in FIG. 15 according to another embodiment. The subterranean drilling system 1100 includes a housing 1102 enclosing a downhole drilling motor 1104 (i.e., a motor, turbine, or any other device capable of rotating an output shaft) that is operably connected to an output shaft 1106. A first thrust-bearing apparatus 900<sub>1</sub> (FIG. 15) is operably coupled to the downhole drilling motor 1104. A second thrust-bearing apparatus 900<sub>2</sub> (FIG. 15) is operably coupled to the output shaft 1106. A rotary drill bit 1108 configured to engage a subterranean formation and drill a borehole is connected to the output shaft 1106. The rotary drill bit 1108 is shown as a roller-cone bit including a plurality of roller cones 1110. However, other embodiments may utilize different types of rotary drill bits, such as a so-called "fixed-cutter" drill bit shown in FIGS. 13 and 14. As the borehole is drilled, pipe sections may be connected to the subterranean drilling system 1100 to form a drill string capable of progressively drilling the borehole to a greater depth within the earth.

A first one of the thrust-bearing assemblies 902 of the thrust-bearing apparatus 900<sub>1</sub> is configured as a stator that does not rotate and a second one of the thrust-bearing assemblies 902 of the thrust-bearing apparatus 900<sub>1</sub> is configured as a rotor that is attached to the output shaft 1106 and

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rotates with the output shaft 1106. The on-bottom thrust generated when the drill bit 1108 engages the bottom of the borehole may be carried, at least in part, by the first thrust-bearing apparatus 900<sub>1</sub>. A first one of the thrust-bearing assemblies 902 of the thrust-bearing apparatus 900<sub>2</sub> is configured as a stator that does not rotate and a second one of the thrust-bearing assemblies 902 of the thrust-bearing apparatus 900<sub>2</sub> is configured as a rotor that is attached to the output shaft 1106 and rotates with the output shaft 1106. Fluid flow through the power section of the downhole drilling motor 1104 may cause what is commonly referred to as "off-bottom thrust," which may be carried, at least in part, by the second thrust-bearing apparatus 900<sub>2</sub>.

In operation, drilling fluid may be circulated through the downhole drilling motor 1104 to generate torque and effect rotation of the output shaft 1106 and the rotary drill bit 1108 attached thereto so that a borehole may be drilled. A portion of the drilling fluid may also be used to lubricate opposing bearing surfaces of the bearing elements 906 of the thrust-bearing assemblies 902.

FIG. 18 is a side cross-sectional view of an embodiment of a wire-drawing die 1200 that employs a PDC 1202 fabricated in accordance with the teachings described herein. The PDC 1202 includes an inner, annular PCD region 1204 comprising any of the PCD tables described herein that is bonded to an outer cylindrical substrate 1206 that may be made from the same materials as the substrate 304 shown in FIG. 3A. The PCD region 1204 also includes a die cavity 1208 formed therethrough configured for receiving and shaping a wire being drawn. The wire-drawing die 1200 may be encased in a housing (e.g., a stainless steel housing), which is not shown, to allow for handling.

In use, a wire 1210 of a diameter "d<sub>1</sub>" is drawn through die cavity 1208 along a wire-drawing axis 1212 to reduce the diameter of the wire 1210 to a reduced diameter "d<sub>2</sub>".

While various aspects and embodiments have been disclosed herein, other aspects and embodiments are contemplated. The various aspects and embodiments disclosed herein are for purposes of illustration and are not intended to be limiting. Additionally, the words "including," "having," and variants thereof (e.g., "includes" and "has") as used herein, including the claims, shall be open ended and have the same meaning as the word "comprising" and variants thereof (e.g., "comprise" and "comprises").

The invention claimed is:

1. A polycrystalline diamond compact, comprising:
  - a polycrystalline diamond table, at least an unleached portion of the polycrystalline diamond table including:
    - a plurality of diamond grains directly bonded together via diamond-to-diamond bonding to define interstitial regions, the plurality of diamond grains exhibiting an average grain size of about 50  $\mu\text{m}$  or less;
     - a catalyst occupying at least a portion of the interstitial regions;
     - wherein the unleached portion of the polycrystalline diamond table exhibits a coercivity of about 115 Oe or more;
     - wherein the unleached portion of the polycrystalline diamond table exhibits an average electrical conductivity of less than about 1200 S/m; and
     - wherein the unleached portion of the polycrystalline diamond table exhibits a  $G_{\text{ratio}}$  of at least about  $4.0 \times 10^6$ ; and
     - a substrate bonded to the polycrystalline diamond table.
2. The polycrystalline diamond compact of claim 1 wherein the coercivity is about 115 Oe to about 250 Oe.

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3. The polycrystalline diamond compact of claim 2 wherein the coercivity is about 130 Oe to about 160 Oe.

4. The polycrystalline diamond compact of claim 1 wherein the unleached portion of the polycrystalline diamond table exhibits a specific magnetic saturation of about 15 G-cm<sup>3</sup>/g or less.

5. The polycrystalline diamond compact of claim 4 wherein:

the coercivity is about 115 Oe to about 175 Oe;

the specific magnetic saturation is about 10 G-cm<sup>3</sup>/g to about 15 G-cm<sup>3</sup>/g; and

the unleached portion of the polycrystalline diamond table includes metal-solvent catalyst in an amount of about 3 weight % to about 7.5 weight %.

6. The polycrystalline diamond compact of claim 1 wherein the average electrical conductivity is about 25 S/m to about 1000 S/m.

7. The polycrystalline diamond compact of claim 6 wherein the average electrical conductivity is about 100 S/m to about 500 S/m.

8. The polycrystalline diamond compact of claim 1 wherein the coercivity is about 115 Oe to about 175 Oe.

9. The polycrystalline diamond compact of claim 8 wherein the average electrical conductivity is less than 750 S/m.

10. The polycrystalline diamond compact of claim 8 wherein the unleached portion of the polycrystalline diamond table exhibits a specific magnetic saturation of about 5 G-cm<sup>3</sup>/g to about 15 G-cm<sup>3</sup>/g.

11. The polycrystalline diamond compact of claim 5 wherein the  $G_{\text{ratio}}$  is about  $5.0 \times 10^6$  to about  $15 \times 10^6$ .

12. The polycrystalline diamond compact of claim 5 wherein the unleached portion of the polycrystalline diamond table exhibits a specific permeability less than about 0.10 G-cm<sup>3</sup>/(g-Oe).

13. The polycrystalline diamond compact of claim 1 wherein the catalyst is present in the unleached portion of the polycrystalline diamond table in an amount greater than 0 weight % to about 7.5 weight %.

14. The polycrystalline diamond compact of claim 1 wherein the average grain size is about 30  $\mu\text{m}$  or less.

15. The polycrystalline diamond compact of claim 1 wherein:

the polycrystalline diamond table includes an upper working surface and an interfacial surface bonded to the substrate; and

the average electrical conductivity of the polycrystalline diamond table decreases with distance from the upper working surface toward the substrate.

16. The polycrystalline diamond compact of claim 1 wherein the polycrystalline diamond table is formed from only single layer of polycrystalline diamond extending from an upper working surface of the polycrystalline diamond table to the substrate.

17. The polycrystalline diamond compact of claim 1 wherein the polycrystalline diamond table includes:

a first layer including coarse-sized diamond grains exhibiting a first average grain size; and

a second layer including fine-sized diamond grains exhibiting a second average grain size less than the first average grain size, the first layer disposed between the second layer and the substrate.

18. A polycrystalline diamond compact, comprising:

a polycrystalline diamond table, at least an unleached portion of the polycrystalline diamond table including:
 

- a plurality of diamond grains directly bonded together via diamond-to-diamond bonding to define intersti-



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tial regions, the plurality of diamond grains exhibiting an average grain size of about 30  $\mu\text{m}$  or less; a catalyst occupying at least a portion of the interstitial regions;

wherein the unleached portion of the polycrystalline diamond table exhibits a coercivity of about 115 Oe to about 175 Oe;

wherein the unleached portion of the polycrystalline diamond table exhibits an average electrical conductivity of less than about 1200 S/m; and

wherein the unleached portion of the polycrystalline diamond table exhibits a thermal stability, as determined by distance cut, prior to failure in a vertical lathe test, of at least about 1300 m.

19. A polycrystalline diamond compact, comprising:

a polycrystalline diamond table, at least an unleached portion of the polycrystalline diamond table including: a plurality of diamond grains directly bonded together via diamond-to-diamond bonding to define interstitial regions, the plurality of diamond grains exhibiting an average grain size of about 50  $\mu\text{m}$  or less; a catalyst occupying at least a portion of the interstitial regions, the catalyst is present in the unleached portion of the polycrystalline diamond table in an amount greater than about 0 weight % to about 7.5 weight %;

wherein the unleached portion of the polycrystalline diamond table exhibits a coercivity of about 115 Oe or more;

wherein the unleached portion of the polycrystalline diamond table exhibits an average electrical conductivity of less than about 1200 S/m; and

wherein the unleached portion of the polycrystalline diamond table exhibits a thermal stability, as determined by distance cut, prior to failure, in a vertical lathe test, of about 1300 m; and

a substrate bonded to the polycrystalline diamond table.

20. The polycrystalline diamond compact of claim 18 wherein the polycrystalline diamond table includes a leached region, and wherein the unleached portion of the polycrystalline diamond table is disposed between the substrate and the leached region.

21. The polycrystalline diamond compact of claim 20 wherein the coercivity of the unleached portion of the polycrystalline diamond table is about 130 Oe to about 160 Oe.

22. The polycrystalline diamond compact of claim 18 wherein the coercivity of the unleached portion of the polycrystalline diamond table is about 155 Oe to about 175 Oe.

23. The polycrystalline diamond compact of claim 22 wherein the plurality of diamond grains and the metal-solvent catalyst of the unleached portion of the polycrystal-

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line diamond table collectively exhibit a specific permeability of about 0.060 to about 0.090  $\text{G}\cdot\text{cm}^3/\text{g}\cdot\text{Oe}$ .

24. The polycrystalline diamond compact of claim 23 wherein the polycrystalline diamond table exhibits a  $G_{\text{ratio}}$  of at least about  $30.0 \times 10^6$ .

25. The polycrystalline diamond compact of claim 23 wherein the unleached portion of the polycrystalline diamond table exhibits a  $G_{\text{ratio}}$  of at least about  $5.0 \times 10^6$  to about  $15.0 \times 10^6$ .

26. The polycrystalline diamond compact of claim 19 wherein the polycrystalline diamond table includes a leached region, and wherein the portion of the polycrystalline diamond table is disposed between the substrate and the leached region.

27. The polycrystalline diamond compact of claim 26 wherein the coercivity of the unleached portion of the polycrystalline diamond table is about 130 Oe to about 160 Oe.

28. The polycrystalline diamond compact of claim 19 wherein the coercivity of the unleached portion of the polycrystalline diamond table is about 155 Oe to about 175 Oe.

29. The polycrystalline diamond compact of claim 28 wherein the plurality of diamond grains and the metal-solvent catalyst of the unleached portion of the polycrystalline diamond table collectively exhibit a specific permeability of about 0.060 to about 0.090  $\text{G}\cdot\text{cm}^3/\text{g}\cdot\text{Oe}$ .

30. The polycrystalline diamond compact of claim 29 wherein the polycrystalline diamond table exhibits a  $G_{\text{ratio}}$  of at least about  $30.0 \times 10^6$ .

31. A rotary drill bit, comprising:

a bit body including a leading end structure configured to facilitate drilling a subterranean formation; and

a plurality of cutting elements mounted to the bit body, at least one of the plurality of cutting elements configured as the polycrystalline diamond compact according to claim 1.

32. A rotary drill bit, comprising:

a bit body including a leading end structure configured to facilitate drilling a subterranean formation; and

a plurality of cutting elements mounted to the bit body, at least one of the plurality of cutting elements configured as the polycrystalline diamond compact according to claim 18.

33. A rotary drill bit, comprising:

a bit body including a leading end structure configured to facilitate drilling a subterranean formation; and

a plurality of cutting elements mounted to the bit body, at least one of the plurality of cutting elements configured as the polycrystalline diamond compact according to claim 19.

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